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The Acid-Base Catalysis of the Mutarotation of Glucose in Protium Oxide-Deuterium Oxide Mixtures

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The kinetics of the mutarotation of glucose has been studied in protium-deuterium oxide mixtures (H_2O-D_2O) to ascertain the effect of substituting deuterium for hydrogen upon catalysis by the aqueous solvent, by the acid ion, by an anion base and the conjugate molecular acid. The velocity of the water catalyzed reaction varies linearly with the fraction of heavy glucose and depends only indirectly upon the composition of the water. The velocity of the acid ion catalysis varies linearly with the H_2O-D_2O content. For acetate ion catalysis the rate varies linearly with the fraction of D_2O or of DOAc. Measurements of the temperature coefficient show that the observed decrease in the rate of the water catalyzed reaction arises primarily from a decrease in the entropy of activation (B) and not from an increase in the energy of activation (E_{act}). A method has been devised for determining whether or not any property depends linearly upon the deutero fraction of a substance which may assume two isotopic forms, HX and DX. For the available data on the inversion of sucrose, DX has been identified with D^+. For the present work on the water catalyzed mutarotation of glucose, DX has been identified with heavy glucose.

INTRODUCTION

ACCORDING to present views, acid catalysis[1] depends upon the readiness with which a proton is donated by the catalyst and accepted by the substrate while the converse holds for a reaction catalyzed by bases. The discovery of deuterium permits the testing of these theories by correlating the effects of isotopic substitution upon the component rates with the changes of the acid dissociation constants of the catalyst and substrate. The isotopic effects upon the dissociation constants of acids and bases[2] indicate a still greater kinetic influence.

Hudson[3] showed that the unimolecular rate constant for the mutarotation of α-glucose is identical with that for β-glucose, and that the observed velocity constant $k=k_\alpha+k_\beta$. Nelson and Beegle[4] showed that for pH between 4–6 the catalysis by H^+ and OH^- is negligible and that the specific rotations of α-glucose (+111.2°), of β-glucose (+17.5°) and of the equilibrium mixture (+52.5°) are independent of temperature. Consequently, the ratio (α-glucose)/(β-glucose) $=k_\beta/k_\alpha=K$, is a constant independent of temperature. The observed velocity constant may be expressed $k_{obs}=k_\alpha+k_\beta=k_\alpha(1+K)$; it is obvious that the energy of activation $E_{obs}=E_\alpha=E_\beta$. Since initial, final and equilibrium specific rotations of glucose are the same in light and heavy water it follows that for the ratio $k_\beta/k_\alpha=K$, the constant is independent of medium as well as of temperature. The over-all velocity constant may therefore be used in making comparisons of

[1] Brönsted, Chem. Rev. **5**, 231 (1928).
[2] Lewis, J. Am. Chem. Soc. **56**, 1913 (1934); La Mer and co-workers, unpublished results.
[3] Hudson and Dale, J. Am. Chem. Soc. **39**, 320 (1917).
[4] Nelson and Beegle, J. Am. Chem. Soc. **41**, 559 (1919).

the catalytic efficiencies of light and heavy water since the change of catalyst does not alter the position of equilibrium.

Brönsted and Guggenheim[5] showed that the rate constant k, for simultaneous multiple catalysis could be expressed in the form

$$k = k_{H_2O}C_{H_2O} + \Sigma k_A C_A + \Sigma k_B C_B$$

where k_{H_2O}, k_A and k_B are the specific rate constants of the medium (H_2O), of acids A and of bases B. Although the solvated hydrogen ion, H_3O^+, is the most effective acid (proton donor) nevertheless (undissociated) molecular acids like HAc exhibited catalytic properties. Of the bases (proton acceptors), OH^- is the most effective, but any anion base, as Ac^-, is likewise catalytically effective. They employed the following empirical relations

$$k_A = GK_A^{\ x} \quad \text{and} \quad k_B = GK_B^{\ y}$$

to represent the dependence of catalytic rate upon the dissociation constant K; G is a constant; x and y are 0.25 and 0.34.

TABLE I. *Summary of some previous results for k and E_{act} with the catalysts H_2O, D_2O, H^+ and D^+ at 25°C.**

OBSERVERS	CATALYST	%D_2O	k	EXTRAPOLATION FROM t°C	E_{obs}	E FOR CALC.
K-K	H_2O	0	0.0110	—	17,600	
	H^+	0	0.333	—	19,300	
MH-K-B	H_2O	0	0.0111	various	17,500	17,500
	H^+	0	0.292	"	18,000	18,000
	D_2O	95	0.00350	"	17,800	17,800
	D^+	95	0.177	"	19,300	19,300
P	H_2O	0	0.0109	18		17,000
	D_2O	56	0.00580	18		17,000
	D_2O	95	0.00361	20		17,000
W-J	H_2O	0	0.0105	23.3		16,800
	H^+	0	0.29	23.3		20,000
	D_2O	98	0.0027	23.3		16,800
	D^+	98	0.22	23.3		20,000

K-K, Kilpatrick and Kilpatrick;[6] MH-K-B, Moelwyn-Hughes, Klar, Bonhoeffer;[7] P, Pacsu;[8] W-J, Wynne-Jones.[9]

[5] Brönsted and Guggenheim, J. Am. Chem. Soc. **49**, 2554 (1927).

* Throughout this paper, the symbols H^+ and D^+ will be used as abbreviated formulas for the solvated proton and deuteron.

[6] Kilpatrick and Kilpatrick, J. Am. Chem. Soc. **53**, 3698 (1931).

[7] Moelwyn-Hughes, Klar and Bonhoeffer, Zeits. f. physik. Chemie **A169**, 113 (1934); Moelwyn-Hughes, ibid. **B26**, 272 (1934).

[8] Pacsu, J. Am. Chem. Soc. **55**, 5066 (1933); **56**, 745 (1934).

[9] Wynne-Jones, J. Chem. Phys. **2**, 381 (1934).

PREVIOUS WORK IN $H_2O - D_2O$

Early reports of other investigations on the mutarotation of glucose in $H_2O - D_2O$ are presented in Table I for comparison below. These data, originally reported at various temperatures, have been calculated to 25°C for convenient comparison. The uncertainty involved in the extrapolation, where E_{act} has not been determined, is probably negligible.

MATERIALS AND PROCEDURE

Heavy water was recovered from glucose solution by distillation in vacuum and redistilled from alkaline permanganate. An Eimer and Amend C.P. grade of glucose, $[\alpha]_D = 109°$, was employed.

The velocity was followed polarimetrically[10] with an electric sodium vapor lamp and 200 mm water jacketed polarimeter tubes. For the earlier experiments[11] in 10–60 percent D_2O the polarimeter tube was of 14 cc capacity with a glass inner tube. For later experiments a similar tube of 2-cc capacity was used.

The effect of a difference in temperature between the room and the thermostat upon the temperature of the polarimeter tube was determined and the correction to be applied found to be 0.0076° per degree difference. The Beckmann thermometers in the thermostat were compared with B.S. calibrated thermometers to the nearest 0.01°. The temperature for parallel runs is reproducible to 0.02°.

For experiments with the 14-cc polarimeter tube the solutions were prepared volumetrically and with the 2-cc tube they were prepared gravimetrically, except for uncatalyzed runs when a trace of hydrochloric acid required to give a slightly acid solution (pH 4–5), was measured from a calibrated Beckmann capillary.

Solutions were made up by weight in a glass-stoppered weighing bottle and the reaction initiated by adding α-glucose. Solutions contained 0.10 g/cc of glucose.

At the conclusion of an experiment the density of the solution was determined with a calibrated 1-cc weight pipette and corrected for buoyancy.

[10] A Goerz polarimeter with Lippich system, 0° to 360° in ¼°, verniers to 0.01° diametrically opposed, was employed.

[11] Hamill and La Mer, J. Chem. Phys. **2**, 891 (1934).

The D_2O content of the medium was calculated on the basis of the specific gravity of the water, determined before the run, allowance being made for exchange and for dilution.

Generally 60 or 80 observations were made at regular intervals of 15, 30 or 60 seconds.

Calculations

The velocity constants were calculated analytically rather than graphically using the Guggenheim[12] method. Four observations are required for a single velocity constant and each observation is employed only once.

If the processes of isotopic exchange and mutarotation were coincident, or occurred independently at nearly equal rates, the proportion HG/DG would alter continuously and k_{obs} would drift. It is important, therefore, to examine the data critically for a possible drift of the velocity constants in heavy water. The slow velocity at 15°C in 93 percent D_2O yielded a large number of observations. The constants for different ranges, by three methods, appear in Table II. If any drift occurs it is less than 0.1 percent in k. We conclude, therefore, that exchange occurs much more rapidly than mutarotation.

Table II. *Velocity constants by different methods at 15.30°C in 93 percent D_2O.*

Method	t(min)			No. Obs.	$k(10)^6$
Guggenheim	13–46, 212–245; 77–110, 276–309			136	1165
Final observation	13.....32	276....295		40	1167
	33.....52	296....315		40	1164
	77.....96	411....430		40	1166
	97....116	431....450		40	1167
Repeated middle observation	77....116	276....315	475....514	120	1167
	13.....52	212....251	411....450	120	1165

Isotopic Equilibria

Glucose should exhibit five exchangeable hydrogen atoms.[7] Three experiments in 30 percent D_2O and one in 80 percent D_2O yielded an average value of 0.7 for the isotopic exchange equilibrium constant for the reaction (1).[13]

$$\tfrac{1}{5}C_6H_{12}O_6+HDO = \tfrac{1}{5}C_6H_7D_5O_6+H_2O \quad K=0.7. \quad (1)$$

These experiments were followed by a general investigation of isotopic exchange with carbohydrates,[14] in which the experimental technique and methods of calculation developed for the glucose exchange were employed and described. For tetramethylglucose which possesses only one exchangeable hydrogen atom, it was found that $K=K_1=0.83$.

$$(Me)_4GH+HOD = (Me)_4GD+HOH \quad K=0.83. \quad (2)$$

This constant is important for the interpretation of the results of the present work.[15]

The isotopic equilibrium constants for several exchange reactions have been collected in Table III for later reference.

Table III. *Isotopic equilibrium constants.*

$H_2O+D_2O=2HDO$	$K_1=3.27$	(1)[16]
$2D^++H_2O=2H^++D_2O$	$K_2=15.4$	(2)[17]
$D^++H_2O=H^++HDO$	$K_3=(K_1K_2)^{\frac{1}{2}}=7.1$	(3)
$HOAc=H^++OAc^-$	K_4	(4)
$DOAc=D^++OAc^-$	K_5; $K_4/K_5=3.2$	(5)[17, 18]
$H_2O=H^++OH^-$	K_6	(6)
$D_2O=D^++OD^-$	K_7; $K_6/K_7=6$	(7)[19]
$HOAc+HDO=DOAc+H_2O$	$K_8=K_4/K_5K_3=0.45$	(8)

Experimental Results and Discussion

Water catalysis in H_2O-D_2O

The data for the spontaneous water reaction may be consistently accounted for either by attributing the change in velocity constant over the range H_2O-D_2O only to variation in basicity of the solvent (3) or alternately to variation in acidity of the substrate (4). Corresponding to these extreme views the following equations may be written:

$$k_{obs}=k_{H_2O}C_{H_2O}+k_{HDO}C_{HDO}+k_{D_2O}C_{D_2O}, \quad (3)$$

$$k_{obs}=k_{0_{H_2O}}-(k_{0_{H_2O}}-k_{0_{D_2O}})F_{DG}. \quad (4)$$

The symbols have the significance: $k_{0_{H_2O}}=55k_{H_2O}$, $k_{0_{D_2O}}=55k_{D_2O}$, $F_{DG}=(DG)/\{(DG)+(HG)\}$. In order to test the former hypothesis it is only

[12] Guggenheim, Phil. Mag. **2**, 538 (1926).

[13] It is important to remember that this constant is composite and is actually $(K_1K_2K_3K_4K_6)^{1/5}$, where subscripts refer to position in the molecule.

[14] Hamill and Freudenberg, J. Am. Chem. Soc. **57**, 1427 (1935).

[15] Hamill and La Mer, J. Chem. Phys. **4**, 144 (1936).

[16] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

[17] La Mer and Korman, by e.m.f. measurements, unpublished.

[18] La Mer and Chittum, conductance results, unpublished.

[19] Abel, Bratu and Redlich, Zeits f. physik. Chemie **A173**, 353 (1935).

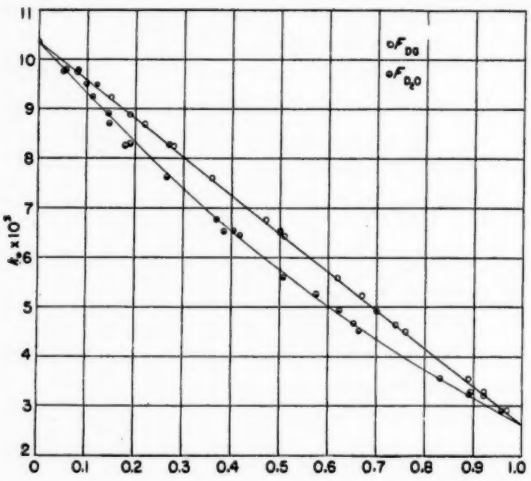

FIG. 1. Water catalysis in H_2O-D_2O at 24.97°C.

necessary to observe whether or not a constant value is obtained for k_{HDO} since all other quantities in (3) are known. To test the second hypothesis, (4) is employed to calculate F_{DG} and, since $(DG)/(HG)=F_{DG}/(1-F_{DG})$, from this to evaluate the isotopic equilibrium constant for Eq. (5).

$$K=(DG)(HOH)/(HG)(HOD). \qquad (5)$$

Both tests have been made and both k_{HDO} and K remain constant over the entire range of H_2O-D_2O concentrations.[11, 15]

Of these two hypotheses, that expressed by (4) is preferred for the following reasons. If the reaction rate depends only upon the basic strength of the catalyst, then according to the general relation $k_b=G(1/K_A)^x$ the molecules H_2O and D_2O should be equally effective catalysts since $K_B=1/55$ for both. Also, the average value of the constant for (5) calculated from these data, $K=0.84$, is confirmed by an earlier finding from isotopic exchange equilibrium measurements which gave, as the result of a single experiment, $K=0.83$ for tetramethylglucose.[14] It is to be expected that F_{DG} will be determined by the isotopic exchange constant for tetramethylglucose since the exchange constant for glucose is composite whereas that for tetramethylglucose refers to that hydrogen atom which is prototropically involved in mutarotation.

By substituting for F_{DG} in (4) its equivalent in (6)

$$\frac{0.84(HOD)/(HOH)}{1+0.84(HOD)/(HOH)}=F_{DG} \qquad (6)$$

and for $k_{0_{H_2O}}$ and $k_{0_{D_2O}}$ the values 0.01040 and 0.00273, respectively, it is possible to obtain k_{calc}. The numerical data have been published[15] and need not be repeated here. On the basis of k_{obs} the a.d. in k_{calc} is 1.2 percent. For twenty-three determinations of $k_{0_{H_2O}}$ at 25°C the a.d. is 0.9 percent.

This comparison is expressed graphically in Fig. 1; the lower line gives the locus of points for k_{obs} *vs.* $\Delta s/0.1079$, where Δs is difference in specific gravity between heavy and normal water.

Acid catalysis

The experimental data for the acid catalyzed reaction, Table IV and Fig. 2, fit the equation $k=0.311-0.084F_{D_2O}$, the a.d. being only 1.3 percent as compared to an a.d. from the mean of 1.6 percent for 17 determinations of k_{H^+} at 25°C.

It is unlikely that there is any real dependence of $k_{H^+D^+}$ upon the D_2O content of the medium. The system is complex, isotopically, since there are several isotopic varieties of substrate, of acid and perhaps of intermediate complex.

It is of interest to contrast with this reaction the acid catalyzed inversion of sucrose[20, 21, 22] in H_2O-D_2O for which the ratio of velocity constants k_{D^+}/k_{H^+} is greater than two at 25°C and varies in a decidedly nonlinear manner with

TABLE IV.

$\frac{\Delta s}{0.1079}$	No. Acid Concentrations	$k_{H^+D^+}$	$\frac{\Delta s}{0.1079}$	No. Acid Concentrations	$k_{H^+D^+}$
Hydrogen ion catalysis in H_2O-D_2O at 24.97°C			*Hydrogen ion catalysis in H_2O-D_2O at 24.97°C*		
0.000	17	0.311	0.840	2	0.241
0.035	2	0.307	0.890	2	0.240
0.108	3	0.300	0.960	3	0.230
0.145	3	0.298	1.000		(0.227)
0.265	2	0.286	*Hydrogen ion catalysis in H_2O-D_2O at 34.85°C*		
0.507	3	0.271			
0.51	1	0.267			
0.54	1	0.267	0.831	3	0.723
0.60	1	0.259	0.840	2	0.680
0.663	5	0.256	0.890	1	0.709
0.831	2	0.241	0.960	3	0.660

[20] Moelwyn-Hughes and Bonhoeffer, Naturwiss. **22**, 174 (1934).
[21] Gross, Suess and Steiner, Naturwiss. **22**, 662 (1934).
[22] Hamill and La Mer, J. Chem. Phys. **4**, 294 (1936).

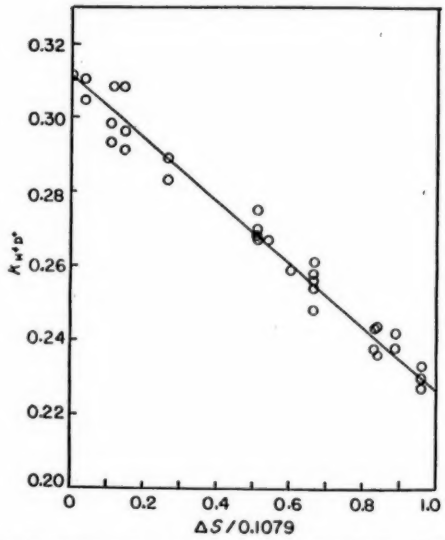

FIG. 2. Hydrogen ion catalysis in H_2O-D_2O at 24.97°C.

change in D_2O content of the medium. If it be assumed, in analogy with the explanation successfully applied to the variation of k_0 in H_2O-D_2O, that the velocity constant varies linearly with the fraction of some substance which may be present in two isotopic forms, and that the following equilibrium exist

$$HX+HDO=DX+H_2O \qquad (7)$$

it is possible to calculate the isotopic equilibrium constant K_x for the assumed equilibrium. The data, together with the results of the calculation appear in Table V. The exchange constant for

TABLE V. *Inversion of sucrose in H_2O-D_2O at 25°C.*

$k_{H^+D^+}/k_{H^+}$	1.00	1.15	1.33	1.67	2.01	(2.10)
F_{D_2O}	0.000	0.444	0.671	0.90	0.981	1.000
K_x		0.11	0.12	0.10	0.14	

the reaction (8)

$$H^++HDO=D^++H_2O \qquad (8)$$

has been determined recently by La Mer and Korman as 0.14. (Table III.) For this reaction, therefore, the velocity constant varies nearly, if not quite, linearly with $(D^+)/(H^+)+(D^+)$. This explanation, as a first approximation, indicates the comparative simplicity of a reaction catalyzed specifically by hydrogen ion as compared to a reversible prototropic reaction and deserves further study.

INFLUENCE OF TEMPERATURE

The integrated Arrhenius Eq. (9) where B and E_{act} are taken as constants independent of temperature,[23] accounts for the present results within the experimental error.

TABLE VI. *E_{act} and B for the water catalyzed reaction in H_2O-D_2O.*

$\frac{\Delta s}{0.1079}$	t°C	$k_0(10)^5$	No. RUNS	E_{act}	B
0.000	15.30	401	2		
				16,860	10.36
0.000	24.97	1040	23		
				16,650	10.21
0.000	34.85	2559	5		
				16,710	10.25
0.831	24.97	356	1		
				16,650	9.74
0.831	34.85	876	1		
0.890	24.97	324	1		
				16,910	9.89
0.890	34.85	809	1		
0.929	15.29	116.5	2		
				17,090	10.00
0.929	34.85	769	2		
1.000	24.97	(273)		16,960	9.85

TABLE VII. *E_{act} and B for the hydrogen ion catalyzed reaction in H_2O-D_2O.*

$\frac{\Delta s}{0.1079}$	t°C	$k_{H^+D^+}$	No. RUNS	E_{act}	B
0.000	16.84	0.126a	2		
				19,230	13.6
0.000	24.98	0.313	2		
0.000	24.97	0.311	16		
				19,450	13.7
0.000	34.85	0.891	10		
				19,400	13.7_0
0.831	24.97	0.240	2		
				20,370	14.3
0.831	34.85	0.722	3		
0.840	24.97	0.236a	3		
				18,900	13.2
0.840	34.85	0.862	3		
0.840	16.84	0.100a	3		
				19,300	13.5
0.840	34.85	0.703	3		
				19,560	13.7
0.840	24.97	0.244	1		
0.890	24.97	0.240	2		
				20,000	14.0
0.890	34.85	0.709	1		
0.960	24.97	0.230	3		
				19,490	13.6
0.960	34.85	0.660	3		
1.000	24.97	(0.227)		19,500	13.63

(a) A single portion of acidulated water was used for all runs in this group.

[23] See, however, V. K. La Mer, J. Chem. Phys. **1**, 289 (1933); J. Am. Chem. Soc. **55**, 1739 (1933).

$$\log k = B - E_{act}/2.3RT. \quad (9)$$

The observed difference of 250 calories in E_{act} for $k_{0_{H_2O}}$ and $k_{0_{D_2O}}$ may be due to experimental error. Although Moelwyn-Hughes finds a corresponding difference of 300 calories (see Table I) it may not be considered a confirmation of the difference reported here since his values of E_{act} are nearly 1000 cal. larger than ours. The observed difference for $k_{0_{H_2O}}$ and $k_{0_{D_2O}}$ is to be accounted for then, as due mainly to change in B, involving the entropy of activation, rather than in E_{act}.

The small difference in E_{act} for k_{H^+} and k_{D^+} is well within the experimental error whereas Moelwyn-Hughes found E_{act} for k_{D^+} to be the larger by 1300 cal. In general the results of the present work disagree with those of Moelwyn-Hughes and of Pacsu, but agree with those of Wynne-Jones.

Since the values found in the present work for E_{act} in H_2O and D_2O for both water and hydrogen ion catalysis (Tables VI and VII) are considerably lower than others which have been previously reported (Table I), it is important to decide between the two sets of values. As the simplest means for a comparison with previous work, velocity constants for the spontaneous water reaction at different temperatures are collected in Tables VIIIA and VIIIB. E_{act} has been calculated for all on the basis of the 0.15°C value of Nelson and Beegle.[4] The results are observed to fall into two groups; the selection of this point as a common basis for comparison is fair to all results since neither group of values for E_{act} shows a drift with temperature although there is a significant difference in values between members of the two groups. The present results are considered to be well confirmed by the others in Table VIIIA.

Neither Pacsu nor Moelwyn-Hughes, Klar and Bonhoeffer mention control of pH within the limits of the catalytic minimum.[4] We attribute their higher results to a failure to adequately control pH.[11, 24]

TABLE VIII. *Calculated values of B and E_{act} on the basis of recent determinations of water catalysis.*

t°C	k_0	E_{act}	B	OBSERVERS
		A		
0.15	0.00078			N-B
15.29	0.00401	16,800	10.32	LM-H
18	0.00530	16,800	10.32	B-G
23.3	0.0089	16,900	10.40	W-J
24.97	0.01040	16,900	10.39	LM-H
25	0.0104	16,900	10.39	N-B
30	0.01634	16,700	10.23	LM-H
34.85	0.02559	16,900	10.39	LM-H
37	0.0301	16,700	10.24	N-B
		16,800	10.32	
		B		
0.15	0.00078			N-B
18	0.00546	17,200	10.64	P
19.65	0.00646	17,200	10.64	M-K-B
20	0.00660	17,100	10.56	K-K
25	0.01098	17,200	10.64	K-K
29.74	0.01751	17,300	10.71	M-K-B
39.86	0.04533	17,400	10.79	M-K-B

B-G, Brönsted and Guggenheim;[5] K-K, Kilpatrick and Kilpatrick;[6] M-K-B, Moelwyn-Hughes, Klar and Bonhoeffer;[7] LM-H, La Mer and Hamill; N-B, Nelson and Beegle;[4] P, Pacsu;[8] W-J, Wynne-Jones.[9]

Acetate ion catalysis

The individual k's for acetate ion catalysis (Table IX, Fig. 3) agree, on the average, within

TABLE IX. *Acetate ion catalysis and molecular acetic acid catalysis in H_2O-D_2O at 24.97°C.*

$\frac{\Delta s}{0.1079}$	No. Ac^- Concentrations	$k_{Ac^-}(10)^4$	No. HAc Concentrations	$k_{HAcDAc}(10)^4$
0.000	5	566	1	57
0.313	4	464	1	45
0.466	1	405		
0.43			2	36
0.652	4	355	2	33
0.919	2	255	2	25
1.000		(238)		(22)

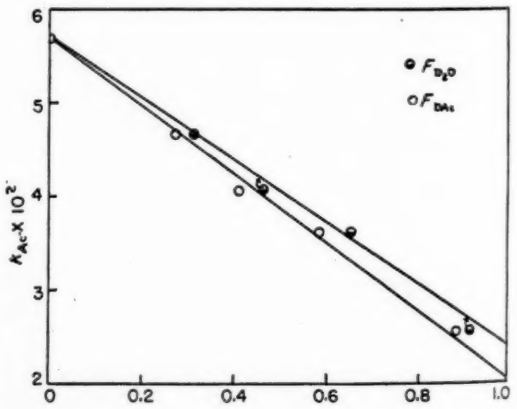

FIG. 3. Acetate ion catalysis in H_2O-D_2O at 24.97°C.

[24] Wynne-Jones (Chem. Rev. **17**, 115 (1935)) has also offered the same explanation.

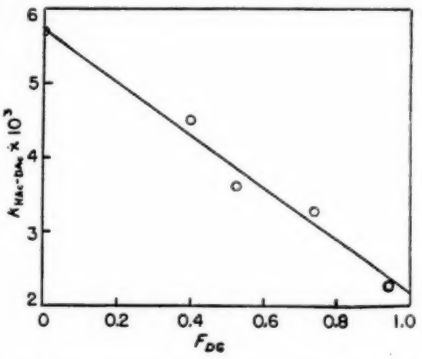

FIG. 4. Molecular acetic acid catalysis in H_2O-D_2O at 24.97°C.

2.5 percent of the values calculated from Eq. (10) and within 3.3 percent of the values calculated from Eq. (11).

$$k_{Ac^-} = 0.0567 - 0.0340 F_{D_2O}, \qquad (10)$$

$$k_{Ac^-} = 0.0567 - 0.0362 F_{DAc}. \qquad (11)$$

The precision of the experimental results alone is not sufficient to permit a choice between these equations.

Catalysis by molecular acetic acid

It may only be concluded that the ratio k_{Ac^-}/k_{HAc} is roughly 10/1 in D_2O as well as in H_2O, and is in marked contrast with the ratio 1.37 for k_{H^+}/k_{D^+}. The results of these measurements are described by the equation $k = 0.0057 - 0.0034 F_{DG}$ (see Fig. 4).

General acid-base catalysis

The isotope effect upon the Brönsted equations, $k_A = GK_A^x$ and $k_B = GK_B^y$, is summed up in Table X. Although two catalytic constants are insufficient to determine x or y with any considerable precision, they suffice for comparisons in H_2O and D_2O.

It is seen that x and y are not significantly affected by the media H_2O and D_2O and that as a result of this the ratio of the G's is simply $G_{H_2O}/G_{D_2O} = k_{0H_2O}/k_{0D_2O}$ for base catalysis and $G_{H_2O}/G_{D_2O} = k_{H^+}/k_{D^+}$ for acid catalysis. We may write,

TABLE X. *The influence of isotopes upon the constants of the equation* $k = GK^x$.

k_B	B	K_B	G	y
0.01040 / 55	H_2O	1/55		
			$8.7(10)^{-4}$	0.384
0.0567	$Ac^-(H_2O)$	$1/1.8(10)^{-5}$		
0.00273 / 55	D_2O	1/55		
			$2.3(10)^{-4}$	0.382
0.0238	$Ac^-(D_2O)$	$1/5.7(10)^{-6}$		
k_A	A	K_A	G	x
0.311	H_3O^+	55		
			0.11	0.27
0.0057	HAc	$1.8(10)^{-5}$		
0.227	D_3O^+	55		
			0.07	0.29
0.0022	DAc	$5.7(10)^{-6}$		

$$\frac{k_{B,\,H_2O}}{k_{B,\,D_2O}} = 3.8\left[\frac{K_{B,\,H_2O}}{K_{B,\,D_2O}}\right]^y = 3.8\left[\frac{K_{A,\,D_2O}}{K_{A,\,H_2O}}\right]^y,$$

$$\frac{k_{A,\,H_2O}}{k_{A,\,D_2O}} = 1.37\left[\frac{K_{A,\,H_2O}}{K_{A,\,D_2O}}\right]^x.$$

Since the ratio $K_{A,\,D_2O}/K_{A,\,H_2O}$ reaches a maximum of 1 for hydrogen ion, and a minimum of $\frac{1}{6}$ for H_2O (considering only the usual catalysts), other acids occupying intermediate positions in order of acid strength,[25] one infers that $k_{B,\,H_2O}/k_{B,\,D_2O}$ reaches its maximum for $B = H_2O$, D_2O and that $k_{A,\,H_2O}/k_{A,\,D_2O}$ reaches its minimum for $A = H_3O^+$, D_3O^+. It will be of interest to observe whether or not similar results obtain for other reactions.

A Summary of Relations on Acid-Base Catalysis in H_2O-D_2O; The Effect of Temperature

H_2O-D_2O	$k = 0.01040 - 0.00767 F_{DG}$
H^+D^+	$k = 0.311 - 0.084 F_{D_2O}$
	$k = 0.0567 - 0.0340 F_{D_2O}$
$Ac^-(H_2O-D_2O)$	
	$k = 0.0567 - 0.0362 F_{DAc}$
HAc − DAc	$k = 0.0057 - 0.0034 F_{DG}$
H_2O	$\log k = 10.25 - 16{,}710/2.3RT$
D_2O	$\log k = 9.85 - 16{,}960/2.3RT$
H^+	$\log k = 13.73 - 19{,}400/2.3RT$
D^+	$\log k = 13.66 - 19{,}500/2.3RT$

[25] Halpern, J. Chem. Phys. 3, 456 (1935), La Mer and Korman (unpublished).

The Raman Spectra of the Deuteromethanes

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The four deuteromethanes were prepared. Their vibrational Raman spectra were photographed under high dispersion. A total of 20 lines were analyzed. A discussion, in the light of the general theory, is given of a sequence of observed overtones.

INTRODUCTION

THE structure and properties of the methane molecule are of particular interest because it is the simplest of the series of carbon hydrogen compounds. Its infrared and Raman spectra have been reported by a number of investigators and the theory of the structure of the molecule has also been extensively studied.[1] With the discovery of deuterium it became possible to prepare and study the deuteromethanes. These isotropic molecules are exceptionally well suited to the investigation of the isotopic effect on polyatomic molecules because of their simple structure. The infrared absorption spectrum of CH_3D has been investigated by Barker and Ginsberg,[2] and Dadieu and Engler[3] have investigated the Raman spectrum of CD_4. There are, of course, five isotopic methanes depending upon the substitution of hydrogens by deuterium, and it is the purpose of this investigation to study the Raman spectra of all these compounds.

Rosenthal[4] has developed a theory of the isotopic effect for such polyatomic molecules in terms of a general potential energy function involving five constants, the final expression for the normal vibrations being given in terms of the potential energy constants of normal methane and mass factors. Dennison and Johnston[5] using the four frequencies of ordinary methane, as observed in the infrared and Raman spectra, and also making use of the rotation-vibration interaction of normal methane, have calculated the frequencies of the four deuteromethanes. It should be observed that several important inaccuracies enter into these calculations which preclude hope of any exact agreement between calculated and observed frequencies. Because of the lack of knowledge concerning the anharmonicity of the vibrations, the observed frequencies have been used in the theory to calculate force constants as if they were the normal vibrations with zero amplitudes. As a result the frequencies calculated by Dennison and Johnston for the deuteromethanes are not the normal vibrations. Also, the observed frequencies of these deuteromethanes differ from the normal vibrations by the anharmonicity corrections. In general, these anharmonicity corrections are of such magnitudes that agreement between calculated and observed frequencies for the deuteromethanes cannot be expected within about five percent.

The object of this investigation has been to determine carefully the Raman spectra of gaseous deuteromethanes.

EXPERIMENTAL

Preparation of compounds

Monodeuteromethane was prepared by the reaction of methyl iodide and deuterium oxide in the presence of an aluminum-mercury couple according to the following reaction,

$$3CH_3I+3D_2O+Al-Hg \xrightarrow{\text{couple}} 3CH_3D+Al(OD)_3+3HgI.$$

Vacuum distilled methyl iodide and 99 percent pure deuterium oxide were used. The aluminum-mercury couple was prepared in the usual manner by the action of 0.5 percent $HgCl_2$ solution on clean aluminium clippings. The couple was washed with 95 percent alcohol and then vacuum dried to remove traces of hydrogen compounds,

[1] Angström, Ofversigt af Kang Vetenskaps.—Akad. Forh. **47**, 331 (1890); Coblentz, Investigations of Infra-red Spectra; J. P. Cooley, Astrophys. J. **62**, 73 (1925); D. M. Dennison, Astrophys. J. **62**, 84 (1925); V. Guilleman, Ann. d. Physik **81**, 173 (1926); Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929); S. Bhagavantam, Ind. J. Phys. **6**, 595 (1932); S. C. Beswas, Phil. Mag. **13**, 455 (1932).

[2] Barker and Ginsburg, J. Chem. Phys. **3**, 668 (1935).

[3] A. Dadieu and W. Engler, Naturwiss. **23**, 355 (1935).

[4] J. Rosenthal, Phys. Rev. **45**, 538 (1934).

[5] Dennison and Johnston, Phys. Rev. **47**, 93 (1935).

principally water. Methyl iodide and deuterium oxide were vacuum distilled onto the couple. The reaction proceeded as soon as the mixture reached room temperature. The gas formed was allowed to pass through a dry ice trap in order to catch the water vapor and other condensables and was stored finally in a glass bulb. A drawback of this method of preparation is that the couple reacts with the water, resulting in a deuterium impurity of about ten percent. This was ascertained by determining the pressure of the gas in a known volume at liquid-air temperature where the methane has a vapor pressure of 8 cm so that the excess pressure beyond this was due to deuterium, and at room temperature where the pressure is due to the methane and deuterium. The amount of impurity was determined approximately since it did not in any way interfere with the interpretation of the results, for the Raman frequencies of deuterium are known from the work of Teal and MacWood.[6] Dideutero- and trideuteromethane were prepared in a similar fashion, using methylene iodide and bromoform, respectively.

Tetradeuteromethane was prepared by a catalytic process in the gas phase.[7] Deuterium and carbon dioxide were allowed to react in the presence of a supported Ni catalyst at a temperature of 310°C, according to the reaction,

$$CO_2+4D_2=CD_4+2D_2O.$$

The deuterium gas was prepared electrolytically from pure deuterium oxide. Commercial solid carbon dioxide was used as the source of carbon dioxide, the gas being purified by passage through 95 percent sulfuric acid. Deuterium and carbon dioxide were passed over the catalyst at 310°C in a four to one ratio. The rates were controlled by the electric current in the cell generating deuterium, and by a bubble-counter in the case of the carbon dioxide. The water formed was removed in a solid carbon dioxide trap and the methane collected as a liquid at liquid-air temperature. When enough liquid methane was collected, the reaction was stopped and the methane allowed to evaporate at −80°C (CO_2) into a large glass storage bulb. The only impurity that can be expected in this case is a small amount of carbon dioxide. This impurity again causes no difficulty since its spectrum is well known from the work of Langseth and Nielson.[8]

Spectroscopic technique[6]

The Hilger E-1 quartz spectrograph which was used in this investigation was thermostated at 32±0.05°C and barostated at 740±0.1 mm. Imperial eclipse plates were used and found to be exceptionally fast. It should be mentioned, however, that for intensity measurements they would be of little value due to their high contrast. A Raman tube of the Wood type, 60 cm long and 2.5 cm in diameter was used. A platinum diaphragm plated with platinum black at the front end of the tube served to eliminate scattered light. The exciting light was obtained from three low pressure "Hanovia" 2537 mercury arcs, 133 cm long and 1 cm in diameter, bent into the shape of closed S's. These arcs give, according to the manufacturers, about 85 percent of their radiation in the λ2537 resonance line, making them ideal sources for Raman work. The arcs were firmly held against the Raman tube by a polished aluminum reflector bound around them. A difficulty attending these arcs is the rapid production of ozone, due, no doubt, to considerable radiation in the λ1849 region. This ozone between the reflector and the Raman tube, unless eliminated from the region, will reduce the intensity of the exciting light considerably. A moderate stream of nitrogen, flowing through this space, was found to decrease this effect. In order to prevent fogging of the plate by the Rayleigh scattered radiation, it was partially absorbed by the vapor of a small amount of mercury placed in the spectrograph.

For the Raman spectra of CH_3D, CH_2D_2, and CHD_3 the pressure of the gas under investigation was about two atmospheres, because of the limited amounts of gas available. For CD_4, a pressure of 5 atmospheres was used. The exposure times in all cases ranged between 150 and 200 hours.

As a reference spectrum, the iron arc was used, photographed immediately below and above the

[6] G. Teal and G. MacWood, J. Chem. Phys. **3**, 760 (1935).
[7] B. Neumann and K. Jacob, Zeits. f. Elektrochemie **30**, 557 (1924).
[8] A. Langseth and J. Nielson, Nature **130**, 92 (1932).

TABLE I. *A comparison of previously observed Raman frequencies with those observed in this work.*

MOLECULE	PREVIOUSLY OBSERVED	THIS PAPER	
N_2	2328.3[9]	2328.4	−0.1
	2331.0[10]	2328.3	0.0
		2328.9	−0.6
CO_2	1388.9[8]	1388.4	0.5
		1389.2	−0.3
		1388.7	0.2
	1285.6	1285.8	−0.2
CH_4	2914.8[11]	2914.2	0.6
CHD_3	2141.0[9]	2141.1	−0.1
CD_4	2108.0[9]	2108.1	−0.1

Raman spectrum with the aid of a Hartman diaphragm at the end of the exposure. The error in the measurement of the Raman lines was about ± 0.5 cm^{-1}. This is substantiated by the results presented in Table I where a comparison of the frequencies of known molecules observed in this investigation with their accepted values is given.

RESULTS

Since the methane molecules have tetrahedral structure, each will have nine normal vibrations, but for reasons of symmetry some of these are identical. CH_4 and CD_4 have tetrahedral symmetry and they will have a non-degenerate symmetrical vibration of frequency, ν_1, a doubly degenerate symmetrical vibration of frequency, ν_2, and two triple degenerate antisymmetrical vibrations of frequencies ν_3 and ν_4.[12] CH_3D and CHD_3 have only a threefold symmetry axis, and therefore there will be three non-degenerate parallel vibrations of frequencies ν_1, ν_{3c}, ν_{4c}, and three doubly degenerate perpendicular vibrations of frequencies ν_2, ν_{3ab}, ν_{4ab}. The molecule CH_2D_2 has only a twofold axis of symmetry and, hence, all the nine normal vibrations are non-degenerate and we designate the frequencies ν_1, ν_{2a}, ν_{2b}, ν_{3a}, ν_{3b}, ν_{3c}, ν_{4a}, ν_{4b}, ν_{4c}.

In Table II are given the observed frequencies of the five methanes compared with those calculated by Dennison and Johnston.[5] The calculated values are enclosed in parentheses.

[9] Unpublished work of MacWood and Teal, see also reference 6, p. 763.
[10] F. Rasetti, Proc. Nat. Acad. Sci. **15**, 234, 515 (1929).
[11] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).
[12] J. Rosenthal, Phys. Rev. **46**, 730 (1934).

TABLE II. *Vibrational frequencies of the isotopic methanes.*

CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
ν_1 (2914.2)	ν_1 unobs. (2944)	ν_1 2139.0 (2141)	ν_1 2141.1 (2101)	ν_1 2084.7 (2061)
ν_2 (unobs.)	ν_2 unobs. (1460)	ν_{2a} 1332.9 (1317)	ν_2 1299.2 (1286)	ν_2 unobs. (1075)
		ν_{2b} unobs. (1424)		
$2\nu_2$ (3071.5)	$2\nu_2$ 2921.7	$2\nu_{2b}$ 2916.4	$2\nu_2$ 2512.4	$2\nu_2$ 2108.1
		ν_{3c} unobs. (2227)		
	ν_{3c} 2199.5 (2183)	ν_{3a} 2974.2 (2969)	ν_{2c} unobs. (2992)	
ν_3 (3022.1)	ν_{3ab} unobs. (3013)	ν_{3b} unobs. (3013)	ν_{3ab} 2268.6 (2222)	ν_3 2258.0 (2227)
	ν_{4ab} 1330.1 (1300)	ν_{4a} 1285.6 (1228)	ν_{4ab} unobs. (994)	
	$2\nu_{4ab}$ unobs.	ν_{4b} 1033.1 (1019)	$2\nu_{4ab}$ 1963.4	
ν_4 (unobs.)				ν_4 unobs. (987)
	ν_{4c} unobs. (1151)	ν_{4c} unobs. (1082)	ν_{4c} unobs. (1020)	
	$2\nu_{4c}$ 2314.8	$2\nu_{4c}$ 2179.6	$2\nu_{4c}$ 2092.8	

Rotational structure of CD_4 was observed associated with ν_3. It was, however, too weak for measurement.

DISCUSSION

There are several interesting points which require investigation and which will have a bearing on the theory of the Raman effect. The following overtones are observed though the fundamentals are not observed with one exception,

CH_4 $-2\nu_2$.
CH_3D $-2\nu_2$, $2\nu_{4c}$.
CH_2D_2 $-2\nu_{2b}$, $2\nu_{4c}$.
CHD_3 $-2\nu_2$, $2\nu_{4c}$, (ν_2 observed but very weak).
CD_4 $-2\nu_2$.

There is the further problem of the nonoccurrence of the following fundamental frequencies,

CH_4 $-\nu_2$, ν_4.
CH_3D $-\nu_1$, ν_2, ν_{2b}, ν_{4c}.
CH_2D_2 $-\nu_{2b}$, ν_{3b}, ν_{3c}, ν_{4c}.
CHD_3 $-\nu_{3c}$, ν_{4ab}, ν_{4c}, (ν_2, weak).
CD_4 $-\nu_2$, ν_4.

The occurrence of the lines corresponding to the various normal vibrations is determined by the activity which depends entirely on symmetry

considerations. Placzek, Tisza and others[13] have shown that for molecules having T_d, C_{3v} and C_{2v} symmetry, corresponding to CX_4, CX_3Z and CX_2Z_2, all the vibrations are active in the Raman effect. Then, since all the vibrations are active, the observability of the lines corresponding to the various normal vibrations will be determined by the intensity of the Raman wave-lengths.

In order to calculate the intensity of the various vibrational lines, we require a knowledge of the vibrational wave functions and the dependence of the polarizability on the normal coordinates.[13] The latter relationship is in general unknown and the wave functions are taken to a first approximation as the product of the wave functions of harmonic oscillators.

The polarizability may be developed in terms of the normal coordinates, about the equilibrium position, giving

$$\alpha(q)=\alpha^0+\sum_j \alpha_j^0 q_j+\tfrac{1}{2}\sum_{j,\ k}\alpha_{jk}^0 q_j q_k+\cdots,$$

where $\alpha_j^0=(\partial\alpha/\partial q_j)_0$, $\alpha_{jk}^0=(\partial^2\alpha/\partial q_j\partial q_k)_0$, etc.

and the q's are the normal coordinates.

If we form the matrix elements of α, we obtain for the vibrational transitions,

$$(\alpha)^{v_j}_{v_j+1}=(v_j+1)^{\frac{1}{2}}[\alpha_j^0 C_j+\tfrac{1}{6}(v_j+1)\alpha_{jjj}^0 C_j^3+\cdots],$$

$$(\alpha)^{v_j}_{v_j+2}=\tfrac{1}{2}((v_j+1)(v_j+2))^{\frac{1}{2}}\alpha_{jj}^0 C_j^2+\cdots,$$

where $$C_j=(h/8\pi^2\nu_j)^{\frac{1}{2}}.$$

Now since the square of the matrix elements of the polarizability determines the intensity and since these are functions of C_j which are small quantities, it may be concluded that the overtones, $n\nu_j$, and combination tones, $n\nu_j+m\nu_k$, depending on C_j^n and $C_j^n C_k^m$, will in general be considerably weaker than the fundamentals. In special cases, where the quantity α_j vanishes or is very small, this rule may be changed, that is, the fundamental will not be observed and the first overtone may or may not be observed, depending upon the magnitude of α_{jj}. In connection with the magnitude of α_j it seems reasonable to assume that for vibrations along valence bonds the change in the polarizability will be a maximum, as for ν_1 of CH_4 and CD_4, since as the hydrogen atoms move in toward the carbon nucleus the polarizability will decrease approaching that of neon as a limit for the united atoms. For vibrations such as ν_2 or ν_4 of CH_4 and CD_4 in which the hydrogen atoms are moving on the surface of a sphere or an ellipsoid the change will be small as the carbon-hydrogen distance will change but little. The ν_2 and ν_4 vibrations for the other methanes, only overtones of which are observed, will be described by a motion similar to ν_2 or ν_4 of CH_4 and CD_4 and so would be expected to satisfy the above criterion.

Another phenomenon of interest in connection with the occurrence of overtones is quantum-mechanical resonance between certain of the energy states of the molecule due to accidental degeneracy or approximate coincidence of the levels corresponding to the various vibrations.[14] The extent of resonance and the distribution of intensity in the lines corresponding to resonating levels have been found to be functions of the separation of the levels, of the frequency and of the anharmonicity of the vibrations.[15] It should be observed that resonance will not in any way account for the nonappearance of the fundamental of the overtone taking part in the phenomenon.

The appearance of the overtones mentioned in the preceeding paragraph may be aided by resonance and in particular the appearance of $2\nu_{4ab}$ of CHD_3 can be attributed to resonance with ν_1. However, it hardly seems probable that all of these overtones are due to resonance since close coincidence with other fundamentals does not seem to occur in all cases and such a regularity as the appearance of these overtones is probably due to the same effect in all cases. We therefore are inclined to the view that they are due to the α_{jj}'s being large and the nonappearance of the fundamentals to the α_j's being small.

The anharmonicity is another effect that must be considered. The effect of anharmonicity is to increase or decrease the intensity of overtones

[13] G. Placzek, Leipziger Vortrage, p. 71 (1931); Zeits. f. Physik **70**, 83 (1931); Placzek and Teller, Zeits. f. Physik **81**, 209 (1933); L. Tisza, Zeits. f. Physik **83**, 48 (1933); E. B. Wilson Jr., J. Chem. Phys. **2**, 482 (1934); Phys. Rev. **45**, 706 (1934).

[14] E. Fermi, Zeits. f. Physik **71**, 250 (1931); D. Dennison, Phys. Rev. **41**, 304 (1932).

[15] G. Placzek, *Handbuch der Radiologie*, VI, Vol. 2 (1934), pp. 316–323.

and combination tones depending upon the type of perturbation. As this is unknown, all that can be said is that the maximum effect will be of the order of the nonlinear terms in the development of the polarizability. The effect will therefore be small in general.

In conclusion, it may be said that the appearance of Raman lines is governed by the following factors: symmetry of the molecule, the effect of the motion of the hydrogens relative to carbon on the magnitude of α_j, and α_{jj}, resonance interaction of nearly commensurable frequencies, anharmonicity of the vibrations involved. In the case of the isotopic methanes, the nonappearance of fundamentals may be attributed to the circumstance that α_j is very small. The appearance of overtones may be due either to the fact that α_{jj} is large, or to resonance, or their combined influence. The effect of anharmonicity should be small, but cannot be predicted.

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An Analytic Method of Interpretation of Electron Diffraction Photographs of Gases*

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An analytic procedure to be used in the interpretation of electron diffraction photographs for gases is developed. The experimentally determined positions of the maxima and minima are employed to solve directly for the interatomic distances through successive approximations. The method is then generalized so as to be applicable to molecules in which rotations or large oscillations about a bond are permitted. As a test, three sets of data which have already been published are recalculated yielding somewhat altered values for the molecular parameters. New diffraction photographs of propane are analyzed. It is pointed out that the number of theoretical intensity curves which must be computed to obtain the correct structure is thereby greatly reduced.

I

IN the analysis of electron or x-ray diffraction photographs of gases, it has been customary to plot I *versus* x, of the function

$$I=k\sum_{ij}\psi_i\psi_j\frac{\sin l_{ij}x}{l_{ij}x}, \qquad (1)$$

where

$\psi_{i\ \text{x-rays}}=f_i(x)$ the structure factor for atom i

$\psi_{i\ \text{electrons}}=4\pi(Z_i-f_i(x))/x^2$

$x=4\pi\sin(\theta/2)/\lambda.$

$l_{ij}=$distance between the ith and jth atoms,

for various values of the parameters l_{ij}, and to choose those values for which the corresponding curve shows the best fit with the experimentally determined intensity distribution both in general shape and in the positions of the maxima and minima. Those investigators[1] working with electron beams found it advantageous to use various simpler functions for the form of ψ_i than the one given above.[2] Justification for these has been adequately discussed in the literature. It is evident that even with the simplest form of ψ_i ($\approx Z_i$), the labor involved in calculating the numerous curves for molecules having only three doubtful shape parameters becomes very great. Were it desirable to investigate three different values for each l_{ij} in such a case, it would be necessary to plot 3^3 curves for each conceivable model to take care of all possible combinations. Then, to obtain the best fit, it might be essential to interpolate between the curves. For more complicated molecules the necessary number of computations rises very rapidly. In practice, therefore, one must make frequent use of the assumption of the constancy of interatomic distances and angles for the same group of atoms in different molecules and can investigate only "reasonable" models.

* Contributions from Gates Chemical Laboratory, California Institute of Technology, No. 540.

[1] L. Pauling and L. O. Brockway, J. Chem. Phys. **2**, 867 (1934); L. R. Maxwell, S. B. Hendricks and V. M. Mosley, ibid. **3**, 699 (1935).

[2] N. F. Mott, Proc. Roy. Soc. **A127**, 658 (1930).

One may regard the determination of molecular structure from electron diffraction photographs as consisting of two parts; the first, in which the form of the model is determined, the second, in which exact values for the interatomic distances are obtained. As has been indicated, in the procedures used heretofore, both parts necessitated the plotting of many intensity curves, their shape being the deciding factor in the first and the exact positions of the maxima and minima in the second. The radial distribution method[11] is a step towards the reduction of the somewhat personal factor in the analysis leading to the correct model; the following analytic procedure in which the experimentally determined $x_{\max}$ and $x_{\min}$ values are directly employed eliminates the stochastic approach to the evaluation of the interatomic distances. This method is particularly applicable to situations wherein a large number of sharp maxima and minima appear.

For the purposes of the discussion assume that the visually estimated ring diameters correspond to extremal values of the function[3]

$$\sum_{ij} Z_i Z_j \frac{\sin l_{ij}x}{l_{ij}x}. \tag{2}$$

Their positions (x_κ) are given analytically by the equation

$$\sum_{ij} Z_i Z_j \left(\cos l_{ij}x_\kappa - \frac{\sin l_{ij}x_\kappa}{l_{ij}x_\kappa} \right) = 0. \tag{3}$$

If there are at least as many experimental values of x_κ as there are unknown *independent* l_{ij}'s, it is possible to determine the latter by solving the set of κ simultaneous equations given by (3). Provided the type of model chosen is the correct one, the values so obtained should be reasonable and should be in agreement with the x_κ's not used in the calculation. Unfortunately, the exact solution of the above set does not appear feasible.[4]

This will be even more evident when it is recalled that the number of l_{ij}'s occurring in (3) is, except for the simplest structures, greater than the number of independent parameters, if the obvious symmetry of the molecule is considered. Some of these will, therefore, be expressed as functions of the fewer remaining ones.

Results can be deduced through successive approximations if use is made of a table of empirical covalent radii.[5] Choose reasonable values for the independent l_{ij}'s ($l_{1,\ 2,\ 3 \ldots n}$). Substitute these in (3) along with the experimentally determined x_κ's. If the former are correct, all of the κ equations will reduce to zero; if not, each will equal some value Y_κ (referred to as *residual*) whose absolute magnitude is directly proportional to the departure from the correct model. In order to find the corrections $\Delta l_{1 \ldots n}$ which must be applied to the chosen $l_{1 \ldots n}$ to make them satisfy (3), differentiate the latter to obtain

$$\Delta Y_\kappa \approx Y_\kappa' - Y_\kappa \approx \sum_n \frac{\partial Y}{\partial l_n} \Delta l_n =$$

$$-\sum_{nij} Z_i Z_j \left[x_\kappa \sin l_{ij}x_\kappa + \frac{\cos l_{ij}x_\kappa}{l_{ij}} - \frac{\sin l_{ij}x_\kappa}{x_\kappa l_{ij}^2} \right] \left(\frac{\partial l_{ij}}{\partial l_n} \right) \Delta l_n, \tag{4}$$

where the new values Y_κ' are to vanish. Since the Y_κ's and the differential coefficients can be readily evaluated,[6] the problem reduces to the solution of a set of linear equations in Δl_n. For higher approximations, the new values of l_n can be used and the process repeated. When more rings are available than there are l_n's, a least-squares treatment of the simultaneous group given by (4) is the logical thing to apply.

One obvious limitation of this procedure can be immediately indicated. Since the functions occurring in (3) and (4) are multivalued, the original guess must not be too distant from the correct values. Another is involved in the initial assumption since it is not yet entirely clear what part of the peak or trough is measured in the

[3] Generalization to the case $\psi_i \neq Z_i$ will be obvious. It will then be necessary to determine $f_i(x)$ in analytic form. See L. Pauling and J. Sherman, Zeits. f. Krist. **81**, 1 (1932). For more accurate work, this will probably become essential.

[4] The expansion of (3) into a series

$$2\sum_{n=1}^{\infty} \frac{(-1)^n n x_\kappa^{2n}}{(2n+1)!} \left(\sum_{ij} Z_i Z_j l_{ij}^{2n} \right)$$

is of no aid whatever. Since the values of l_{ij} are often as large as 5 and those of x_κ as high as 20, the convergence is extremely slow.

[5] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).

[6] A table or large scale plot of the functions ($\cos x - \sin x/x$) and ($x \sin x + \cos x - \sin x/x$) greatly facilitates the calculations.

visual method. It is certain that for peaks which have shoulders or are separated by shallow minima, measurements so obtained do not give quite the correct x_{max}'s. Allowance can be made for this effect when the appearance of the picture as well as the experimental ring diameters are compared with a complete plot of I *versus* x, but it would be highly arbitrary, if indeed it were possible, to introduce a similar allowance in the analytic expressions. One can conclude, therefore, that wherever the interatomic distances are known approximately, the x values of sharp maxima and minima of electron diffraction photographs may be used to obtain them precisely.

Up to the present, the treatment of molecules in which rotations or large oscillations about a bond are permitted has not been very satisfactory.[7] The stochastic procedure which has been applied does not give clear-cut results; the radial distribution method[11] is more reliable. The treatment outlined above can be readily extended to take care of such a situation. Since the time spent by a diffracted electron in the vicinity of the diffracting molecule is small compared to the period of a rotation, the resultant intensity distribution will be similar to one obtained from a mixture of different molecules, each species being present in a concentration proportional to the relative probability of any one specific position in the allowed cycle. Were one to write for the contribution of one species

$$I_s = k' P_s \sum_{ij} Z_i Z_j \frac{\sin l_{ij} x}{l_{ij} x}, \tag{5}$$

where P_s is the probability that the interatomic distances be l_{ij}, the total intensity can be expressed by

$$I = k' \sum_{sij} P_s Z_i Z_j \frac{\sin \alpha_s l_{ij} x}{\alpha_s l_{ij} x}, \tag{6a}$$

where α_s are the factors by which l_{ij} must be multiplied in going from one standard model to any of the others. Consider at first the simple case wherein the interatomic distances of the standard one are known (i.e., l_{ij}, α_s), it being desired to find the relative probability of a number of discrete orientations. Since the observed extremal values occur at

$$\sum_{sij} P_s Z_i Z_j \left(\cos (\alpha_s l_{ij}) x_\kappa - \frac{\sin (\alpha_s l_{ij}) x_\kappa}{(\alpha_s l_{ij}) x_\kappa} \right) = 0, \tag{7a}$$

with the restrictions $s \leqslant \kappa$; $P_s \geq 0$; $\sum_s P_s = 1$, it is only necessary to solve this set of linear simultaneous equations for the P_s's.

A more general procedure may be outlined. Actually both P_s and l_{ij} of (5) vary continuously. Let us write for

$$\begin{aligned} l_{ij} &= f_{ij}(l_n, \theta_{ij}), \\ dn &= N P_1(l_{ij}) dl_{ij} = N P_{11}(\theta_{ij}) d\theta_{ij} \end{aligned} \tag{8}$$

with $$\int_{l_{ij}'}^{l_{ij}''} P_1(l_{ij}) dl_{ij} = 1,$$

where l_n represents the independent parameters of a standard configuration;
θ_{ij} the angle of rotation from the model chosen;
$P_1(l_{ij})$ the probability that dn molecules have their interatomic distances between l_{ij} and $(l_{ij} + dl_{ij})$;
l_{ij}' and l_{ij}'' are the possible extreme values of l_{ij}.

The observed intensity distribution will then be

$$I = N k'' \sum_{ij} Z_i Z_j \int_{l_{ij}'}^{l_{ij}''} P_1(l_{ij}) \frac{\sin l_{ij} x}{l_{ij} x} dl_{ij} \tag{6b}$$

and the condition for a maximum or minimum

$$\sum_{ij} Z_i Z_j \int_{l_{ij}'}^{l_{ij}''} P_1(l_{ij}) \left(\cos l_{ij} x_\kappa - \frac{\sin l_{ij} x_\kappa}{l_{ij} x_\kappa} \right) dl_{ij} = 0. \tag{7b}$$

The above expression has meaning only when the integral can be evaluated. A general form for $P_1(l_{ij})$ which makes this possible is an expansion into a polynomial in l_{ij} or $(1/l_{ij})$.[8] Thus, if the

[7] Symmetrical di-halogen substitution products of ethane have been discussed by: L. Meyer, Zeits. f. physik. Chemie **B8**, 32 (1930)—dielectric constant measurement; R. Wierl, Physik. Zeits. **31**, 366 (1930), Ann. d. Physik **13**, 453 (1932);—electron diffraction; F. Ehrhardt, Physik. Zeits. **33**, 610 (1932)—x-ray diffraction. The only possibilities which have been considered by the latter two investigators are: (a) completely free rotation, or (b) the presence of only two species—*cis* and *trans* forms—in various concentrations.

[8] See Pierce's *Short Table of Integrals* (1929), pp. 46–47; Jahnke-Emde, *Table of Functions* (1933), p. 83 for a table of $\int_0^x (\sin t/t) dt$ for $0 \leq x \leq \infty$. One is not, however, limited to the use of a power series. Functions which may be expressed as a Fourier integral involving undetermined parameters may be equally satisfactory. Since the limits of integration are thus shifted to $\pm\infty$ (the l_{ij}' and l_{ij}'' will now appear explicitly in the functional argument of the integral), the necessary integrations with regard to l_{ij} can be readily performed.

limiting values l_{ij}' and l_{ij}'' are known, as many coefficients of the polynomial can be calculated through the solution of the simultaneous set (7b), as there are experimental x_κ's. Otherwise, the latter equation may be differentiated with respect to the limits of integration, giving

$$\Delta Y_\kappa = \sum_{ij\,l_{ij}''} Z_i Z_j P_1(l_{ij}'') \left(\cos l_{ij}'' x_\kappa - \frac{\sin l_{ij}'' x_\kappa}{l_{ij}'' x_\kappa} \right) \Delta l_{ij}'' - \sum_{ij\,l_{ij}'} Z_i Z_j P_1(l_{ij}') \left(\cos l_{ij}' x_\kappa - \frac{\sin l_{ij}' x_\kappa}{l_{ij}' x_\kappa} \right) \Delta l_{ij}' \tag{9}$$

and the method of successive approximations applied. Then as many coefficients as there are x_κ's less the number of independent unknown l_{ij}'''s may be evaluated. It should be kept in mind that a different $P_1(l_{ij})$ function will be needed for every *independently* varying distance. Since the form of $f_{ij}(l_n, \theta_{ij})$ for any type of model will be known,

$$P_{11}(\theta_{ij}) = P_1(l_{ij}) \partial l_{ij} / \partial \theta_{ij}$$

and, for the particular rotation considered, the potential energy of the molecule at any angle

$$U(\theta_{ij}) = -kT \log P_{11}(\theta_{ij}) \tag{10}$$

can be deduced.

II

To test the applicability of Eqs. (3) and (4), three sets of data which already have appeared in the literature have been recalculated.

Methylene chloride[9]

The two independent parameters taken were the carbon-chlorine and the chlorine-chlorine distances. The effects of the hydrogen atoms can be assumed to be negligible. Ten x_κ values were treated by least squares which gave for the final result

C−Cl	1.78_6A	as contrasted with	1.77±0.03A
Cl−Cl	2.91_3A		2.92±0.02A
(Cl−C−Cl)	$109°_{22'}$		111°±2°

published by the original investigators. The accuracy claimed for the new values cannot be greater than that stated for the old, since the largest source of error is probably inherent in the voltage measurement. That the newly calculated distances will be in better agreement with the given data so far as positions of the ten x_κ values are concerned is, however, emphasized.

Chloroform[8]

The hydrogen terms were again neglected. Thirteen rings were used giving for the final results:

C−Cl	1.78_1A	which are to be compared with those of Sutton and Brockway,	1.78±0.03A
Cl−Cl	2.91_0A		2.93±0.02A
(Cl−C−Cl)	$109°_{34'}$		111°±2°

Phosgene[10]

The three parameters chosen were the C−Cl, Cl−Cl and C−O distances, it being assumed that the molecule is planar. The sums of the covalent radii were taken as the zeroth approximation and eleven rings used in a least-squares treatment of the simultaneous set of Eqs. (4). (The first two rings as well as the ones at $x_\kappa = 12.54$ and 13.51 were discarded for it is obvious that the St. John effect would greatly disturb accurate measurement.) The resulting values gave curve A_1 of Fig. 1, which is to be compared with B, the final curve chosen by the above authors. The lack of an indication of a shoulder at $x_\kappa = 13.51$ eliminates this model. Hence a second approximation (corresponding curve is A_2) was calculated giving for

C−Cl	1.68A	which are to be compared with the published values	1.68A
Cl−Cl	2.86A		2.87A
C−O	1.21A		1.28A
Cl−C−Cl	116°		117°

A_2 is not completely satisfactory yet since the peak at $x_\kappa = 9.34$ has almost disappeared while the one at 13.51 became unduly prominent. The similarity between the two sets of distances clearly indicates, however, the advantages of the straightforward analytic procedure, for it should be recalled that in order to arrive at the values given by Brockway, Beach and Pauling, approximately twenty-five intensity curves had to be plotted. The best agreement with the data (curve B_1) was obtained through another successive

[9] L. E. Sutton and L. O. Brockway, J. Am. Chem. Soc. **57**, 473 (1935).

[10] L. O. Brockway, J. Y. Beach, and L. Pauling, J. Am. Chem. Soc. **57**, 2693 (1935).

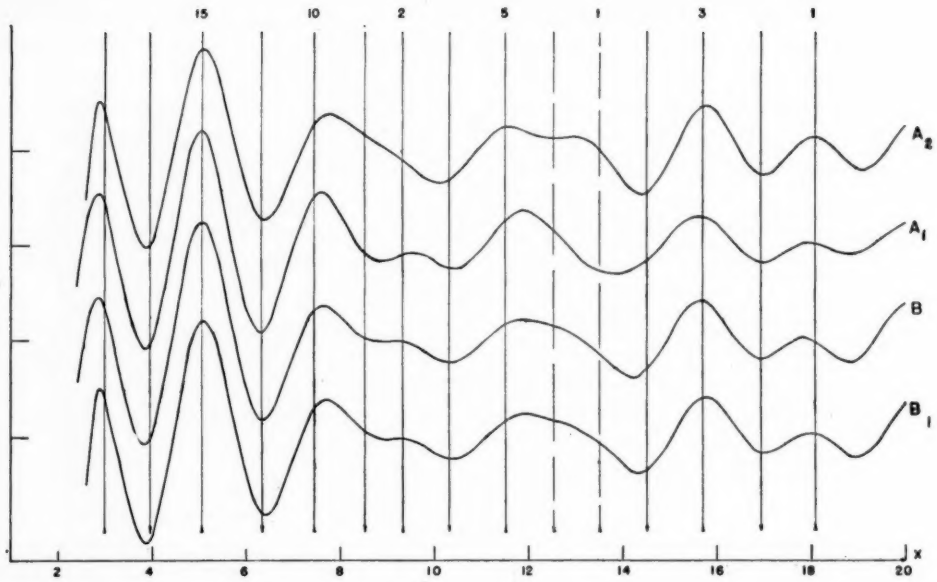

FIG. 1. Calculated intensity curves for phosgene. A_1, first approximation using the covalent radii and 114° for the Cl−C−Cl angle as the zeroth approximation. A_2, second approximation to the above. B, final values of Brockway, Beach and Pauling. B_1, first approximation to B. The numbers at the top of the figure indicate the visually estimated relative intensities of the maxima.

approximation using the distances of B in Eqs. (3) and (4). This resulted in

C−Cl	1.67_4A
Cl−Cl	2.85_3A
C−O	1.26_6A
Cl−C−Cl	$116°_{34'}$

Propane

Electron diffraction pictures of propane (Ohio Chemical Company—twice redistilled) were taken with the hope of obtaining an accurate carbon-hydrogen distance, since the C−H terms in this molecule contribute more than half to the total intensity distribution. The visual appearance of the photographs was that shown in Fig. 2, the relative intensities being an average of estimates by three observers made independently. The photographs were taken at a film distance of 10.43 cm with electrons of wave-length 0.0605 A. The measured values of ring diameters were obtained from five photographs of varying densities, from which the calculated mean x_k's are tabulated in Table I. A five-term radial distribution calculation[11] (Fig. 3) gives indication of several important distances in the molecule none of which can be taken too seriously, however, because of the overlapping of peaks. In the following calculations all the interaction terms were taken into account except those due to H−H when bonded to different carbon atoms. The slight variations in some C−H terms due to rotations of the methyl groups about C−C bonds were also neglected. That these approximations are legitimate can be seen from Fig. 4 A in which the dotted line indicates the theoretical intensity distribution when all factors are considered while the full curve, when the enumerated simplifications are made. The three independent parameters taken were the carbon-hydrogen, carbon-carbon when bonded, and carbon-carbon$_{(end)}$

[11] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).

TABLE I.

	x_K	RELATIVE WTS.	RELATIVE INTENSITIES
1	(3.150)	1	4.0
2	(4.488)	1	3.6
2	6.161	4	8.0
3	7.732	3	2.9
3	9.354	5	3.2
4	11.29	5	0.5
4	12.96	5	1.2
5	15.57	4	0.0
5	17.62	4	0.4

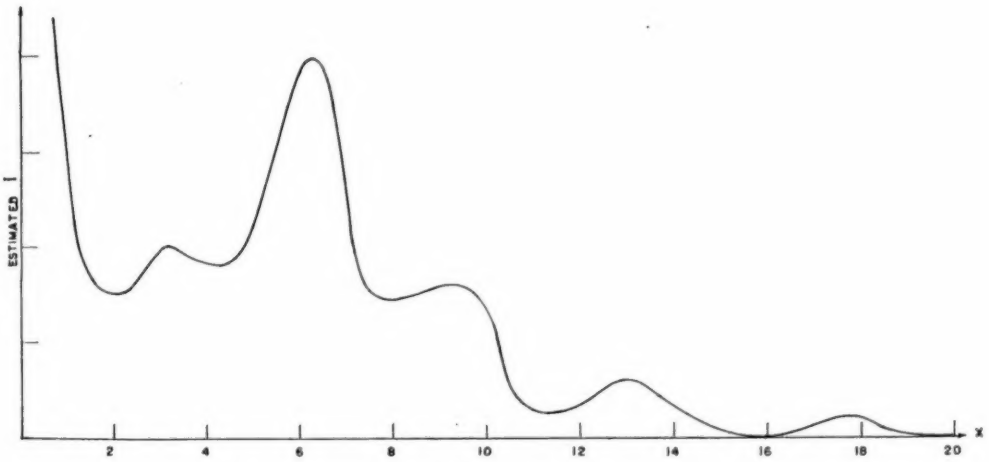

FIG. 2. Visual appearance of electron diffraction photographs of propane.

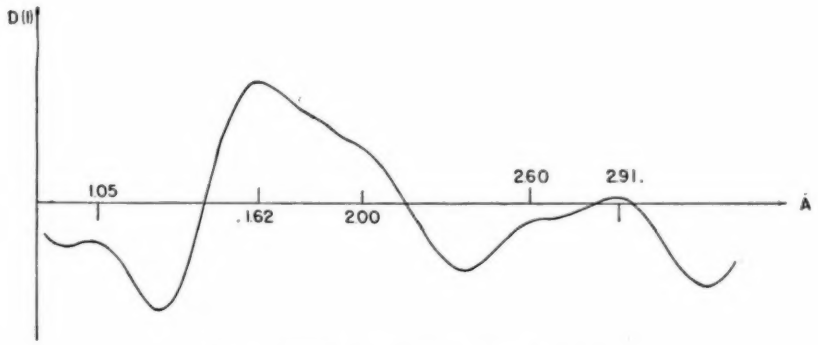

FIG. 3. Radial distribution curve of propane.

distances. The C−C−H angle was assumed tetrahedral throughout. Least-squares treatment of six rings[12] weighted as shown in Table I gave the following distances:

$C-C_{bonded}$	$1.5\mathring{0}_3 \pm 0.02$A
$C-C_{end}$	$2.52_4 \pm 0.03$A
C−H	$1.08_1 \pm 0.02$A
(C−C−C)	$114°_{12'}$

When the last ring is also included in the calculations, an angle of approximately 116° is indicated. In view of the accepted values, these appear somewhat unusual.[13] Further support can be presented in the traditional manner making use of the completed intensity distributions computed by means of equation (2) for a number of models (Fig. 4). Attention is called to curves *A* and *B* which indicate the sensitivity of the intensity to changes in the C−H distance. Although the differences are not highly pronounced, curve *D* is evidently in better agreement both in general form and in the positions of the extremal values than any of the others. The lack of a more distinct first maximum may be due to the neglect

[12] The inner two were not used because of the St. John effect; the last, because of the inherent uncertainty in the measurement because of its faintness.

[13] For propane, R. Wierl (Ann. d. Physik **13**, 453, 1932) gave C−C 1.52±0.05A using the then accepted band spectral value for C−H, 1.10A. In aliphatic hydrocarbons the accepted C−C distance is 1.54A and C−H distance is 1.06A (Table of covalent radii, note 5). The present band spectral value for C−H from the moment of inertia of methane is 1.11A while somewhat different considerations lead to a moment of inertia for methyl deuteride which requires the C−H distance to be 1.093A. See M. Johnson and D. M. Dennison, Phys. Rev. **48**, 868 (1935) and N. Ginsburg and E. F. Barker, J. Phys. Chem. **3**, 668 (1935), respectively. The above discrepancy is discussed by the former authors.

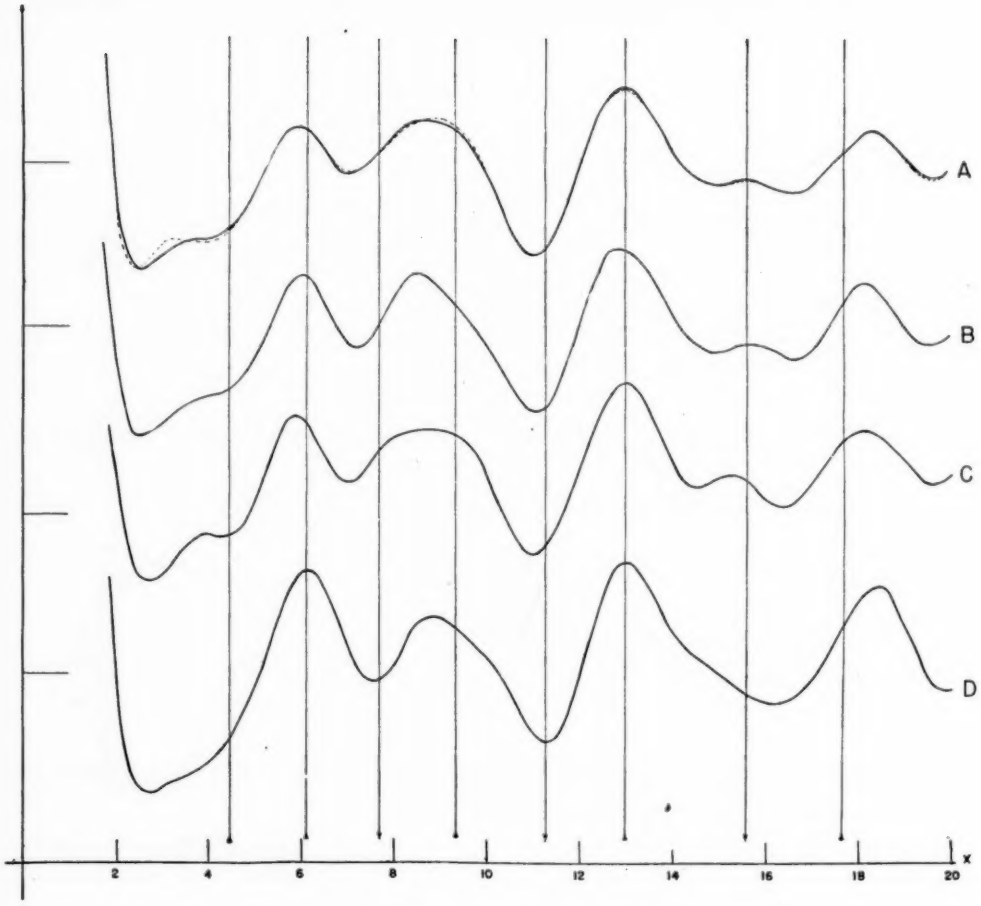

FIG. 4. Calculated intensity curves for models of propane.

A.	C−H 1.05	C−C 1.54	∠C−C−C 109° 28′
B.	C−H 1.06	C−C 1.54	∠C−C−C 109° 28′
C.	C−H 1.06	C−C 1.54	∠C−C−C 112°
D.	C−H 1.08	C−C 1.50	∠C−C−C 114°

of the H−H terms. One must keep in mind, when looking at these curves, that they are to be superposed on a monotonic decreasing function of x because of the presence of the structure factor terms.

Although the present photographs favor strongly the distances quoted, the writer hesitates to present them as final values. Because of the approximations which must be made in the visual method and the subsequent analysis, the inherently smudged diffraction pattern which propane gives does not warrant the use of further successive approximation calculations.

The author acknowledges his indebtedness to Dr. L. O. Brockway for the use of his apparatus and to Professor L. Pauling and Dr. J. Sherman for helpful discussions pertaining to the material here presented.

Absorbing and Reflecting Powers of H_2SO_4 Solutions in the Far Infrared

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The reflecting and absorbing powers, and hence dispersion, of H_2SO_4 solutions were determined as a function of concentration and of wave-length between 50μ and 150μ. Pure H_2SO_4 reflects and absorbs the far infrared less than water as is to be expected from the Debye theory on dipole orientation. A broad band around 60μ, similar to the 60μ band in water, was observed in both concentrated and dilute H_2SO_4. This band appears to be of interatomic origin and possibly a fundamental vibration frequency of the sulphate radical, SO_4, due to bending. The reflecting and absorbing powers of H_2SO_4 solutions are much greater than of pure H_2O or H_2SO_4. This is accounted for by the presence of ions which move in translation to follow the alternations of the electromagnetic waves in the far infrared. The structure of these ions is discussed in reference to other physical properties observed in H_2SO_4 solutions. It is suggested that in adding less than 5 percent water to H_2SO_4 possibly ions of SO_4^{--} and OH_4^{++} might be formed; on further dilution, ions of H^- and H_3SO_5 are formed (hydrated HSO_4^-, with the water making stable six-ring of S−O−H−O−H−O−S); on still further dilution, ions of H^+ and SO_4^{--} become most abundant.

INTRODUCTION

THE measurements of Rubens[1] for the reflecting power of strongly concentrated H_2SO_4, 2 parts H_2SO_4+1 part H_2O, 2 parts H_2O+1 part H_2SO_4 (measured by volume) and of H_2O are given in Table I. Rubens' data show

TABLE I. *Reflecting power.*

SOLUTION	23μ	33μ	52μ	63μ	83μ	94μ	117μ	313μ
H_2SO_4	8.8	7.9	16.9	18.7	17.7	17.7	18.4	21.7%
2 H_2SO_4+H_2O (Vol)	9.2	10.9	19.4	20.6	22.3	—	—	28.8%
2 H_2O+H_2SO_4 (Vol)	8.1	9.6	14.2	17.0	19.0	—	—	26.5%
H_2O	6.5	7.2	9.3	10.6	10.9	11.1	12.7	15.1%

that the reflecting powers of H_2SO_4 solutions are considerably greater than those of pure water or concentrated H_2SO_4. In the present investigation we have increased the number of concentrations and have also measured their absorption thus permitting the dispersion to be calculated.

In Fig. 1 are shown for H_2SO_4 solutions the freezing point, F.P., specific gravity, S.G., specific electrical conductivity, κ, and the viscosity, η.[2] The electrical conductivity of the solutions must of course be attributed to the formation of ions and the Raman spectrum indicates that at least three types of ions exist. In the region of the spectrum investigated, these ions can be expected to follow in translation the alternations of the electromagnetic waves and cause a reflection and absorption considerably in excess to that produced by a turning of the polar molecules or of any active infrared bands.[3]

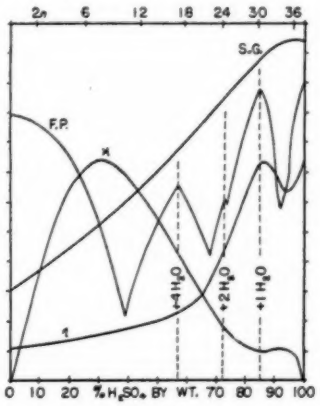

FIG. 1.

Although many physical properties of H_2SO_4 solutions have been studied, the structures of the compounds formed have not been established. The present investigation of the far infrared dispersion of these solutions was undertaken with the hope of giving additional data and a new tool for analyzing the structures of molecules in solutions.

EXPERIMENTAL PROCEDURE

Monochromatic radiations of 52, 63, 83, 100, 117 and 152μ were obtained by the method of reststrahlen with suitable filters for purification. A Wellsbach mantle was used as a source of radiation and the energy was finally detected by a special compensated vacuum thermocouple and

[1] H. Rubens, Verh. d. D. Phys. Ges. **17**, 315 (1915).
[2] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. X, and Fr. Ephraim, *Anorganische Chemie.*
[3] C. H. Cartwright, Phys. Rev. **49**, 101 (1936).

statically-balanced galvanometer which was read by a semi-automatic device. The reststrahlen plates and the specimens were enclosed in a case containing dry air and were changed mechanically from the exterior. For reflection measurements, the solutions were contained in a separate compartment of dry air.

The solutions of H_2SO_4 investigated were 2, 6, 12, 18, 24, 30, 36 and 37.4 normal and were kindly prepared by Dr. Hauss. To facilitate comparison with other investigations, the concentrations expressed as percentage by weight of H_2SO_4 were 9.3, 25.0, 44.0, 59.2, 72.1, 83.4, 96.1 and 100 percent or expressed as percentage by volume of H_2SO_4 they were 5.3, 15.4, 30.0, 43.7, 58.5, 73.3, 92.9 and 100 percent. The most concentrated H_2SO_4 was fuming as it was taken from the bottle but all of the SO_3 gas that would escape at room temperature was allowed to do so in a dry atmosphere before the acid was used for measurements.

For absorption measurements, the solutions were contained between two crystalline quartz plates and the absorption coefficient, $n\alpha$, was calculated by the usual formula:

$$I = I_0^{-4\pi n\alpha d/\lambda}, \qquad (1)$$

where I is the transmission of the cell with the solution of thickness d and I_0 is the transmission of a quartz comparison plate of thickness, 4 mm, having the same thickness of quartz as in the cell. The index of refraction, n, of all the solutions was found to be so nearly that of crystalline quartz for the same wave-lengths, that the loss by reflection from the two surfaces, quartz-liquid and liquid-quartz was negligible. The tabulated thickness, d, of the solutions was determined by measuring the absorbing power of all the solutions at $\lambda = 117\mu$ in a cell of thickness $d = 34.6\mu$. This thickness was too great to give a suitable transmission for shorter wave-lengths so thinner spacers of platinum were used and the thickness, d, was calculated from Lambert's law, formula (1).

The reflection measurements were made on the free surface of the solutions and compared with the reflection from an evaporated tin mirror having 100 percent reflecting power for the wave-lengths used.

The index of refraction, n, was calculated from the reflecting and absorbing power according to the well-known formula:

$$R = 100\frac{(n-1)^2+n^2\alpha^2}{(n+1)^2+n^2\alpha^2}. \qquad (2)$$

Experimental Results

In Table II are recorded the percentage reflection, R, the percentage transmission, T ($T = 100I/I_0$, for a solution of thickness d), the calculated absorption coefficient, $n\alpha$, and the index of refraction, n.

Some of the data in Table II are shown graphically in Figs. 2 and 3, both as a function of wave-length and of concentration.

Discussion

To facilitate a general interpretation of the data in Table II and Figs. 2 and 3, it may be well to recall the different ways in which absorption might occur in the spectral region from 50μ to 150μ: (1) Characteristic absorption bands due to fundamental atomic vibration frequencies of small binding forces, (2) characteristic absorption bands due to combination made up of differences

Table II.

	λ (μ) / ν (cm^{-1})		52 / 192	63 / 159	83 / 120	100 / 100	117 / 85	152 (μ) / 66 (cm^{-1})
H_2O	$d = 19.7\mu$	R	9.2	10.7	11.6	12.0	12.7	13.0%
		T	11.5	14.7	24.4	40.2	49.0	53.3%
		n	0.46	0.49	0.48	0.37	0.34	0.39
		n	1.68	1.77	1.89	2.01	2.04	2.09
$2n$ H_2SO_4	$d = 21.0\mu$	R	10.7	11.8	12.8	13.8	15.1	15.8%
		T	7.0	8.5	15.5	29.2	38.5	44.0%
		n	0.53	0.59	0.59	0.47	0.42	0.47
		n	1.75	1.78	1.87	2.07	2.17	2.19
$6n$ H_2SO_4	$d = 21.4\mu$	R	13.1	14.7	16.2	17.0	18.5	19.7%
		T	3.7	4.7	13.0	23.5	31.2	35.2%
		n	0.64	0.72	0.63	0.54	0.51	0.59
		n	1.85	1.88	2.11	2.27	2.38	2.42
$12n$ H_2SO_4	$d = 21.0\mu$	R	16.8	18.7	19.6	21.0	22.5	23.6%
		T	2.0	3.2	10.3	18.8	26.9	29.9%
		n	0.77	0.82	0.71	0.63	0.58	0.70
		n	2.02	2.13	2.33	2.53	2.66	2.69
$18n$ H_2SO_4	$d = 16.0\mu$	R	19.9	20.2	22.0	23.6	24.5	25.3%
		T	7.0	9.8	18.2	34.1	40.4	45.4%
		n	0.69	0.73	0.71	0.54	0.53	0.60
		n	2.37	2.37	2.54	2.79	2.85	2.89
$24n$ H_2SO_4	$d = 22.4\mu$	R	21.7	22.1	22.1	23.0	24.0	25.4%
		T	2.7	3.2	11.5	20.5	33.0	37.8%
		n	0.67	0.77	0.64	0.56	0.46	0.52
		n	2.53	2.53	2.60	2.73	2.84	2.92
$30n$ H_2SO_4	$d = 20.6\mu$	R	21.9	20.5	20.1	20.6	22.6	24.1%
		T	6.6	7.2	15.1	30.0	40.2	44.9%
		n	0.55	0.64	0.61	0.55	0.41	0.47
		n	2.62	2.46	2.45	2.54	2.74	2.85
$36n$ H_2SO_4	$d = 21.6\mu$	R	13.3	15.9	16.8	17.4	18.3	19.0%
		T	7.4	8.1	19.8	37.5	46.8	51.8%
		n	0.50	0.58	0.49	0.36	0.32	0.37
		n	2.01	2.12	2.25	2.37	2.45	2.47
H_2SO_4	$d = 21.5\mu$	R	8.1	9.7	9.8	10.5	10.6	11.3%
		T	20.5	21.0	38.7	59.5	66.0	71.8%
		n	0.30	0.36	0.30	0.20	0.18	0.19
		n	1.72	1.80	1.84	1.96	1.99	2.00

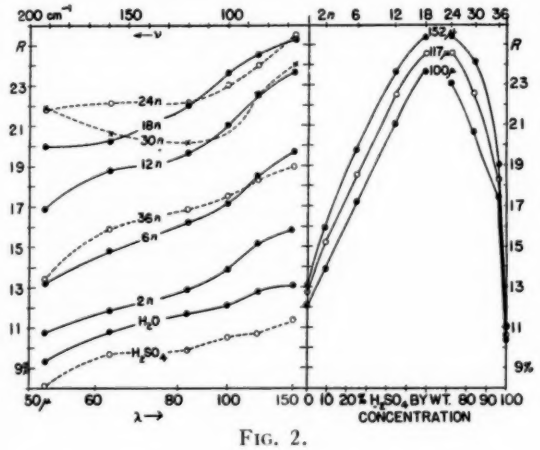

FIG. 2.

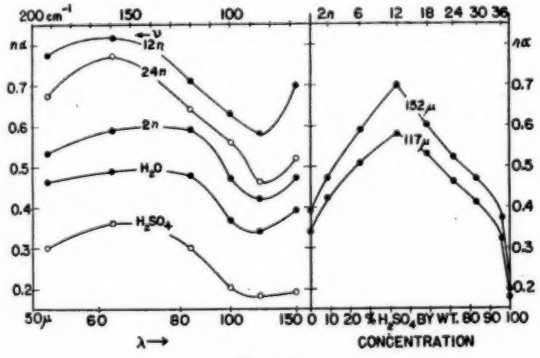

FIG. 3.

of near infrared vibration frequencies, (3) characteristic absorption bands produced by the polar molecules oscillating in a quasi-crystalline structure formed by the intermolecular fields, (4) general absorption due to an orientation of the permanent dipoles, and (5) rather general absorption due to ions following the alternations of the electromagnetic radiation.

1. On 100 percent H_2SO_4

From a study of the absorbing and reflecting powers of more than twenty different liquids,[4] which illustrate the above types of absorption, it was found that the general absorption in water is exceptionally strong. This is explained by the strong permanent dipole, small molecular radius and the low viscosity of liquid water. We should therefore expect pure H_2SO_4 to have a general absorption that is considerably less than that of water. The fact that Rubens (Table I) observed a greater reflecting power for H_2SO_4 than for water suggests that there were ions present. From our data, it can be estimated that the most concentrated H_2SO_4 measured by Rubens was about 36 normal. 100 percent H_2SO_4 is 37.4 normal but it is extremely hygroscopic and difficult to obtain. The most concentrated H_2SO_4 we measured was obtained by allowing fuming H_2SO_4 to give off the dissolved SO_3 gas in a dry atmosphere, so it seems probable that the most concentrated H_2SO_4 we measured contained some dissolved SO_3 rather than H_2O. The especially rapid drop in the curves in Figs. 2 and 3 from 96 percent to 100 percent might therefore be due to SO_3 diluting the H_2SO_4 to give a lower reflecting and absorbing power than would be observed for 100 percent H_2SO_4. On the other hand, although the reflecting and absorbing powers of our strongest acid are less than for water, in view of its being a much more viscous fluid and the molecules having a smaller permanent dipole and a larger radius than water, one might expect still smaller values for the reflecting and absorbing powers for 100 percent H_2SO_4 than we obtained.[5] In fact, our values give a relaxation time of less than 7×10^{-13} sec. and a radius of less than 0.3×10^{-8} cm which are obviously too small and they indicate that in our strongest acid there was a general absorption due to more than an orientation of the permanent dipoles of the H_2SO_4 molecules.

Relative to 100 percent H_2SO_4, we can only conclude that our measurements show qualitatively that the absorbing and reflecting powers of 100 percent H_2SO_4 are less than those of water.

2. Raman spectra results

The Raman spectra of H_2SO_4 solutions have been studied by several investigators.[6] Let us review here the interpretation as given by Woodward and Horner[7] which seems to be generally accepted: (1) The characteristic unsymmetrical Raman band of water begins to show in 75 percent H_2SO_4 solutions (volume concentrations are used) and increases rapidly.

[4] C. H. Cartwright and J. Errera, A. Phys. Chim. U. R. S. S. **3**, 649 (1935).

[5] C. H. Cartwright and J. Errera, Proc. Roy. Soc. **A154** 138 (1936).

[6] Nisi, Jap. J. Phys. **5**, 119 (1929); Woodward, Physik. Zeits. **32**, 212 (1931); R. Rao, Ind. J. Phys. **8**, 123 (1933); S. Rao, Ind. J. Phys. **9**, 195 (1934); R. M. Bell and M. A. Jeppesen, J. Chem. Phys. **3**, 245 (1935); N. G. Pai, Phil. Mag. **134**, 616 (1935).

[7] L. A. Woodward and R. G. Horner, Proc. Roy. Soc. **A144**, 129 (1934).

with dilution. (2) The Raman bands 381, 555, 910, 978, and 1121 cm^{-1} are characteristic of the H_2SO_4 molecule and their intensities diminish rapidly with dilution. (3) The Raman bands 595, 895 and 1036 cm^{-1} are characteristic of an HSO_4^- ion. They are not present in concentrated H_2SO_4 but appear in all solutions and their intensity is a maximum in 25 percent H_2SO_4. (4) The Raman bands 452 and 982 cm^{-1} are characteristic of an SO_4^{--} ion. These bands begin with 50 percent H_2SO_4 and get stronger with dilution.

The Raman spectra are therefore interpreted as successive dissociations from H_2SO_4 to $H^+ + HSO_4^-$ and from HSO_4^- to $H^+ + SO_4^{--}$. The existence of HSO_4^- ions is based on a comparison with the spectra of $KHSO_4$ solutions; but, this does not deny the hypothesis that one molecule of water is combined with HSO_4^- to form an ion of $H_3SO_5^-$. The maxima of the freezing point curve and the viscosity curve in Fig. 1 are strong evidence for the latter as well as the fact that the Raman band of water only appears in more dilute solutions than one molecule of water per molecule of H_2SO_4. In the following we shall assume that ions of $H_3SO_5^-$ rather than HSO_4^- are formed.

Pfund has studied the near infrared reflecting power of several H_2SO_4 solutions[8] and found variations which appear to be in accord with the Raman data. Several of the characteristic bands are seen to be both infrared and Raman active.

3. Characteristic absorption band at about 60μ

The broad absorption band around 60μ in liquid water can be attributed to a movement of the water molecules as a whole in a quasi-crystalline structure.[9, 10] The fact that H_2SO_4 has a band at about 60μ, as shown in Fig. 3, can hardly be interpreted as evidence that the structure of H_2SO_4 is a water molecule loosely attached to a SO_3 molecule, although the transition from SO_3 to H_2SO_4 is continuous with the addition of H_2O to SO_3. Both the Raman and ultraviolet[11] spectra of H_2SO_4 deny such an hypothesis. Since this band is present in both concentrated and dilute solutions, it is probably due to intramolecular rather than intermolecular motions, for the intermolecular fields are a function of concentration. It seems likely that its origin is due to a characteristic frequency of the sulphate radical, SO_4. The intensity of the absorption further suggests that it is a fundamental band rather than due to a combination of near infrared frequencies. That this band has not been observed in the Raman spectra of H_2SO_4 and its solutions might be due to its not being Raman active or it might be due to the experimental difficulties encountered in observing Raman bands of such low frequency. Indeed, the active Raman band in water around 60μ is not mentioned in the Raman investigations on H_2SO_4 solutions.

4. Structure of ions in H_2SO_4 solutions

According to the theory of valency, the two structures of H_2SO_4 and H_2SO_4 plus one molecule of H_2O shown in Fig. 4 should be considered.[12] The stability of $H_2SO_4 \cdot H_2O$, as is shown by the freezing point curve and the viscosity curve in Fig. 1 is rather strong evidence for structures (A) and (A') which form a stable six-ring with the water molecule. The electrical conductivity of the solutions must of course be accounted for by the presence of ions and in Fig. 5 are shown some possible structures as the dilution is increased. It is, however, probable that many of the ions are more than singly hydrated because of the small maximum in the freezing point curve and the sudden change in the index of refraction of visible light[13] for $H_2SO_4 \cdot 2H_2O$. Also the freezing point curve shows that there is a strong tendency for four water molecules to unite with H_2SO_4, although it is not certain that such an association would be stable at room temperature.

Professor Lowry and Professor Pauling have suggested that the structure of $H_2SO_4 \cdot H_2O$ shown in Fig. 6 should be considered. Pauling suggests that both SO_4^{--} and OH_4^{++} would have a tetrahedral structure and intermolecular forces would cause these radicals to form a quasi-

[8] A. H. Pfund, Astrophys. J. **24**, 19 (1906).
[9] M. Magat, J. de physique **5**, 347 (1934).
[10] C. H. Cartwright, Phys. Rev. **49**, 470 (1936).
[11] W. W. Coblentz, Invest. of Infrared Spectra **55**, 100 (1906).
[12] N. V. Sidgwick, *The Electronic Theory of Valency*, p. 286 and p. 195; T. M. Lowry, Nature **121**, 527 (1928); Trans. Faraday Soc. **18**, 285 (1923); Phil. Mag. **45**, 1105 (1923).
[13] J. L. R. Morgan and C. E. Davis, J. Am. Chem. Soc. **38**, 555 (1916).

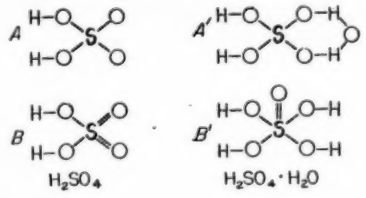

FIG. 4.

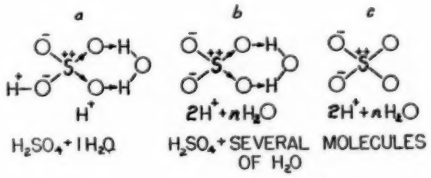

FIG. 5.

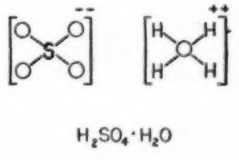

FIG. 6.

crystalline structure in the liquid. The rapid increase in the electrical conductivity curve in Fig. 1 and the reflecting and absorbing powers in Figs. 2 and 3 in the neighborhood of 100 percent H_2SO_4 seem most easily explained in terms of this structure which gives doubly charged ions and therefore a high electrical conductivity in spite of the large viscosity (see formula (4)). However, the behavior of the electrical conductivity as well as the results of Raman spectra (and the breaks at 95 percent concentration in Figs. 2 and 3, if we assume them to be real) indicate that the structure shown in Fig. 6 is probably only present in very strongly concentrated H_2SO_4.

5. Ionic absorption

The large increase in the general reflecting and absorbing powers of the solutions over pure water and H_2SO_4, as shown in Figs. 2 and 3, is due to the presence of ions which follow the alternations of the electromagnetic waves in this region of the spectrum. The wave-length, λ_0 (in μ) for which inertia begins to play a small part in hindering the motion of an ion is given by the formula:[3]

$$\lambda_0 = 1.65 M/\eta r, \tag{3}$$

where M is the molecular weight of an ion of radius r (in A) and η is the specific viscosity of the solution. For the ions in H_2SO_4 solutions λ_0 is probably less than 50μ and their general absorption, as derived from Maxwell's equations, should be given approximately by the relation:

$$n\alpha \approx Ze^2\lambda/n\eta r, \tag{4}$$

where Z is the number of ions of charge e per unit of volume and n is the index of refraction of the solution. Too many factors are involved to draw more than qualitative conclusions at present concerning the number and structure of the ions in as complicated an electrolyte as a solution of H_2SO_4; for, as the Raman spectra show, at room temperature several types of ions are present and their respective concentrations are not well defined as might be suggested by the freezing point curve. From a rather extended study of the reflecting and absorbing powers of different concentrations of electrolytes of HCl, LiCl, NaCl, KCl, KBr, LiI, KI, ZnI_2, $MgSO_4$, and KOH, it was found that the increase in the reflecting and absorbing powers of water by the addition of H_2SO_4 is well accounted for by the formation of two hydrogen ions and one negative ion of SO_4^{--} until a concentration of about 12 normal is reached. Then ions of hydrogen and $H_3SO_5^-$ begin to predominate—a result that is in harmony with the Raman spectra findings. The rapid decrease in the reflecting and absorbing powers as well as the electrical conductivity from 36 normal to 37.4 normal (100 percent H_2SO_4) suggests that ions of OH_4^{++} and SO_4^{--} are first formed when water is added to H_2SO_4 and they reach a maximum concentration in 36 normal solutions. On further dilution, however, they must be replaced by ions of H^+ and $H_3SO_5^-$ to account for the change in electrical conductivity, infrared reflecting and absorbing powers, and the Raman spectra results.

ACKNOWLEDGMENTS

I wish to thank the C. R. B. Educational Foundation for the opportunity of doing research in Belgium and le Fonde National Belge de la Recherche Scientifique for aiding in the construction of the apparatus. I am grateful for the kind hospitality offered by the Université Libre de Bruxelles and particularly Professor Jacques Errera, in whose laboratory these researches were conducted. It is a pleasure to thank Professors J. R. Bates, P. Debye, D. M. Dennison, J. Errera, T. M. Lowry, R. G. W. Norrish and L. Pauling for discussing the results and generously offering suggestions.

Studies of Reactions Induced by the Photoactivation of the Water Molecule. I

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Unbuffered gas free solutions of methyl alcohol have been irradiated with ultraviolet light in the wave-length range longer than 1850A and it is found that reactions involving the methyl alcohol occur, induced by the photoactivation of the water molecule. Gas free water itself is not changed by the irradiation. Products initially obtained in the water-photosensitized reaction are hydrogen as the only gas and a small amount of formaldehyde accounting for 10 to 20 percent of the hydrogen produced. The direct photoactivation of the methyl alcohol leads to its decomposition according to $CH_3OH+(h\nu)=CH_2{:}O+H_2$. The spectral limit for the water-photosensitized reaction is in the neighborhood of 2000A.

A MARKED increase in the absorption of light by water takes place below 2000A. The present communication is concerned with an investigation of reactions, in aqueous solution, induced by the activation of the water molecule with wave-lengths in this region. Our studies have included transformations of carbon monoxide, methyl and ethyl alcohols, formic acid, acetaldehyde, acetone, and diethyl ether, irradiated in gas free solutions. Gas free water, if sufficiently purified, is not itself changed by the irradiations used.

The irradiations have been carried out employing a quartz mercury arc and condensed sparks. The sparks were operated in air or hydrogen by means of a kenetron rectified transformer (20 kv, 50 to 100 ma) and with a 0.02-microfarad condenser in parallel with the spark. The constancy of the irradiations was controlled by a cadmium photoelectric cell connected to a string electrometer. The irradiated solutions were contained in thin walled fused quartz cells and in some experiments in Pyrex cells with windows of crystalline quartz and fluorite.

The reactions were studied by an analysis of the gases produced and by other specific tests. The gas analyses were carried out in a van Slyke gas apparatus. The entire contents of the irradiation cells (usually about 20 cc) were transferred into a 50-cc extraction chamber and the analysis performed in the usual manner. Potassium permanganate was used to liberate oxygen from hydrogen peroxide, sodium hydroxide for the absorption of carbon dioxide, sodium hydrosulfite for the absorption of oxygen, and ammoniacal cuprous chloride for the absorption of carbon monoxide. The composition of the residual gas could be determined by a combustion analysis. Kahlbaum, Merck and Baker's best chemicals used without further purification gave identical results in the irradiations.

For the purification of the water used in preparing the irradiated solutions, distilled water from a Barnstead still was refluxed for extended periods successively in potassium hydroxide-permanganate and in sulfuric acid-potassium dichromate mixtures and the vapor, mixed with oxygen, finally passed through a quartz tube heated to 900°C. This vapor was then condensed in a Pyrex reservoir from which it could be directly transferred into the chamber for filling the cells. The water thus obtained still contains traces of organic impurities as revealed when the water (gas free) is irradiated with ultraviolet light, the decomposition of these impurities taking place with the production of hydrogen and carbon dioxide. With the type of purification described, these gases are reduced to a few micromoles per 1000 cc of water. The water from the Barnstead still gave, under similar treatment, as much as 10 to 20 micromoles of these gases (Fig. 1). The water can be further purified by irradiation with x-rays and this procedure was used in the work with the most dilute solutions.

The purified water was transferred directly to a Pyrex evacuation chamber into which the irradiation cells fitted through ground joints. The chemicals were added, connection made to a water pump, and the dissolved gases removed by the simultaneous warming and shaking of the solution. The solution was then rapidly forced into the irradiation cells by slightly increasing

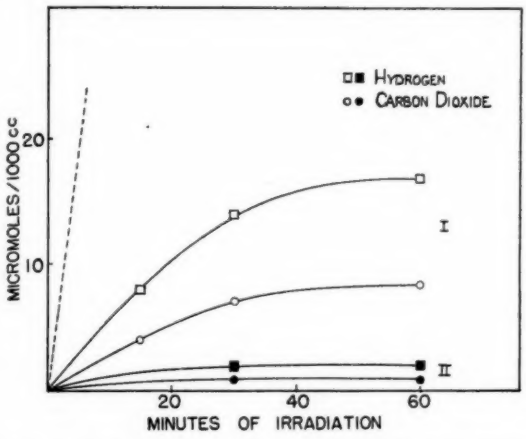

FIG. 1. Water-photosensitized decomposition of organic impurities in water (gas free) by irradiation with ultraviolet light. I: water from tin still; II: water purified as described in text. For comparison, the dotted line shows hydrogen production obtained by irradiating 1 millimolar methyl alcohol. Light source: aluminum spark.

the pressure (with air) on the surface of the liquid. Solutions prepared in this manner yield less than 1 micromole of dissolved gases per 1000 cc of solution. Before being filled, the cells and evacuation chamber could be heated to 500°C for the purpose of removing possible traces of organic material.

We shall begin by describing certain experiments carried out with solutions of methyl alcohol. The water-photosensitized transformation of organic molecules generally is a function of the hydrogen ion concentration, but the present experiments were carried out in unbuffered solution. Besides analyses of the gases produced, supplementary analyses were made for formaldehyde by Hehner's method,[1] the amounts being estimated quantitatively by the use of proper blanks. With this method, the amount of formaldehyde could be estimated to an accuracy of 10 micromoles per liter. The light source was an aluminum spark, the light from which was filtered through 1.4 cm of water. The irradiated solutions were contained in a cylindrical fused quartz cell also 1.4 cm deep and placed 5.4 cm from the spark, and the concentration range 0.001 to 1.0 molar methyl alcohol was studied. Under these conditions, in the initial reactions, the gas produced is essentially hydrogen. (The analyses are not accurate enough to exclude the possibility of the production of small amounts of hydrocarbons.) At the highest concentrations of methyl alcohol there appears to be a trace of carbon monoxide. Formaldehyde is obtained, but at the lower concentrations of methyl alcohol it amounts to only a small fraction of the hydrogen produced. The production of hydrogen and formaldehyde as functions of the methyl alcohol concentration is given in Fig. 2. The values shown are the initial amounts produced per 1000 cc of solution and per minute of irradiation. The reaction time curves remain linear over appreciable ranges in the production of these products. In Fig. 3 is shown the hydrogen production as a function of the time of irradiation for 1 millimolar methyl alcohol.

An estimation of the percentage energy of the chemically active rays absorbed by the irradiated solutions was obtained by interposing, between the light source and the reaction vessel, a similar vessel filled with solutions of methyl alcohol and determining the resulting decrease in the hydrogen produced. These measurements were carried out with 1 millimolar and with 1 molar methyl alcohol in the reaction vessel. The values obtained for the absorption at the lower concentrations of methyl alcohol are not greatly different whether the light intensity is recorded by the effect on 1 millimolar or on 1 molar methyl alcohol and the absorption curve in Fig. 2 was obtained with 1 millimolar methyl

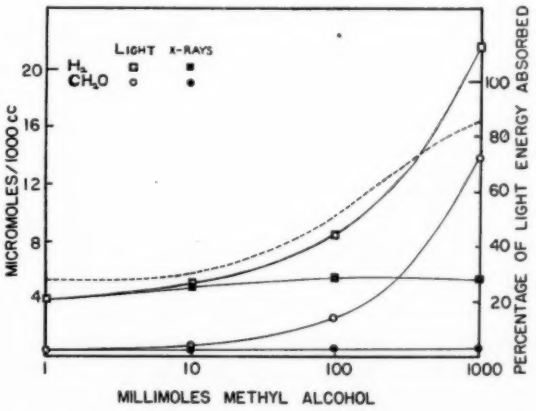

FIG. 2. The production of hydrogen and formaldehyde by the irradiation of solutions of methyl alcohol with light and x-rays. The dotted line represents percentage of effective light energy absorbed in the irradiated solution.

[1] Fulton, C. C., J. Ind. and Eng. Analyt. Ed. Chem. **3**, 199 (1931).

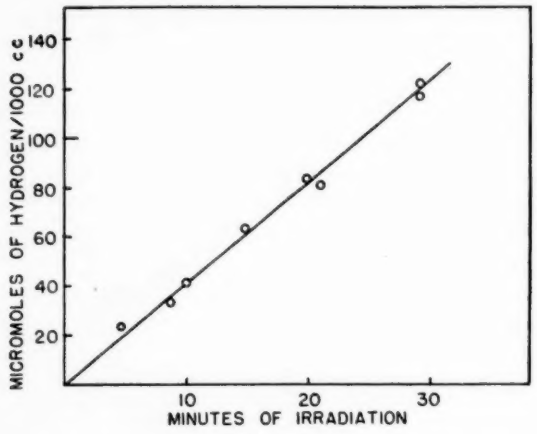

FIG. 3. Production of hydrogen as a function of time of irradiation for 1 millimolar methyl alcohol.

alcohol. The absorption is constant at the lower concentrations of methyl alcohol. Since the absorption is far from complete, it is concluded that this constant absorption represents the absorption of the solvent, while the absorption of the methyl alcohol itself at these concentrations must be comparatively small.

From these results we are led to the conclusion that the reactions occurring at the low concentrations of methyl alcohol cannot be due to the direct photoactivation of methyl alcohol, but are to be attributed to the absorption of the light by the solvent with the subsequent transfer of the absorbed energy to the methyl alcohol. This inference is based in part on the manner in which the hydrogen production varies with the methyl alcohol concentration. From the absorption measurements it follows that the absorption of the chemically active rays by the methyl alcohol itself decreases nearly as the concentration at the low values of concentration used. However, no indication of this decrease in absorbed energy is seen in the hydrogen production, which, on the contrary, at the low concentrations is nearly constant, and has a value which corresponds approximately to the absorption of the light in the water. This view as regards the reaction mechanism is confirmed by a consideration of the qualitative nature of the reactions. The chemical transformations resulting from the photoactivation of the methyl alcohol molecule with wave-lengths within the range here used, were studied by Patat[2] in the vapor phase, and it was found that the initial reaction was essentially the decomposition of the methyl alcohol into hydrogen and formaldehyde. In the present irradiations, at low concentrations of methyl alcohol, the formaldehyde accounts for only a small fraction of the hydrogen produced. At around 10 millimolar methyl alcohol the hydrogen and formaldehyde production both rise rapidly and at approximately equal rates, which is consistent with the observations on methyl alcohol vapor if this rise is considered as representing the direct photodecomposition of the methyl alcohol.

It will be noticed (Fig. 2) that the hydrogen production continues to decrease as the methyl alcohol concentration decreases, even after the point has been reached where the direct photodecomposition should be negligible. A similar decrease is shown by the water-photosensitized decomposition of methyl alcohol for irradiation with x-rays.

The water-photosensitized reactions induced by x-rays have already been the subject of considerable study.[3a–h] A much greater variety of reactions is obtained than with light, but so far as one can judge from the types of analysis used, the reactions occurring are the same in the two cases (light and x-rays) for methyl alcohol. The only gas produced by x-rays is hydrogen, and there is a production of formaldehyde which accounts for the same percentage of the hydrogen as in the case of light. In Fig. 2 are given the quantities of these two molecules obtained per unit of x-ray dosage, chosen arbitrarily so that the hydrogen production agrees with that for light at 1 millimolar methyl alcohol. The curves for light and x-rays agree at the lower concentrations, and deviate where the direct photodecomposition by light becomes appreciable. For x-rays, direct photodecomposition is negligible over the entire range of methyl alcohol concentrations used.

The following experiments were carried out to

[2] F. Patat, Zeits. f. Elektrochemie **41**, 494 (1935).

[3] (a) Fricke H. and S. Morse, Phil. Mag. **7**, 129 (1929); (b) H. Fricke and E. R. Brownscombe, J. Am. Chem. Soc. **55**, 2358 (1933); (c) ibid., Phys. Rev. **44**, 240 (1933); (d) H. Fricke, J. Chem. Phys. **2**, 556 (1934); (e) H. Fricke and E. J. Hart, J. Chem. Phys. **2**, 824 (1934); (f) ibid. **3**, 60 (1935); (g) H. Fricke, J. Chem. Phys. **3**, 364 (1935); (h) H. Fricke and E. J. Hart, J. Chem. Phys. **3**, 596 (1935).

obtain an approximate idea of the spectral limit for the water-photosensitized decomposition of methyl alcohol. The aluminum spark was used as before, and the irradiations made with different concentrations (2.5 to 30 millimolar) of potassium sulfate added to the water in the filter cell; the hydrogen production only was recorded. Although the direct photodecomposition becomes more pronounced at higher sulfate concentrations, still at one millimolar methyl alcohol it remains negligible in comparison with the photosensitized reaction at all concentrations of potassium sulfate used. In Fig. 4 is given the hydrogen obtained at this concentration of methyl alcohol in unit time, plotted logarithmically against the sulfate concentration. The aluminum lines effective in these experiments are those at 1860A, 1934A, and 1990A, and the transmissions of these wave-lengths through the 1.4 cm of potassium sulfate are shown as calculated from the absorption coefficients given by Ley and Arends.[4] As the sulfate concentration is increased, the rate of change of the hydrogen production with sulfate concentration continues to decrease, and at the highest sulfate concentration is smaller than that which follows from the transmission of 1934A. The limit of the water-photosensitized reaction is therefore at a wave-length longer than this value. For comparison,

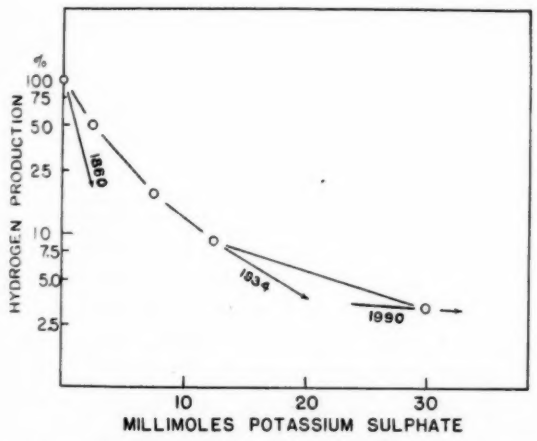

FIG. 4. Hydrogen production as a function of the concentration of potassium sulfate in filter cell. Light source: aluminum spark. The transmissions of certain of the aluminum lines are shown.

[4] H. Ley and B. Arends, Zeits. f. physik. Chemie **15**, 311 (1931).

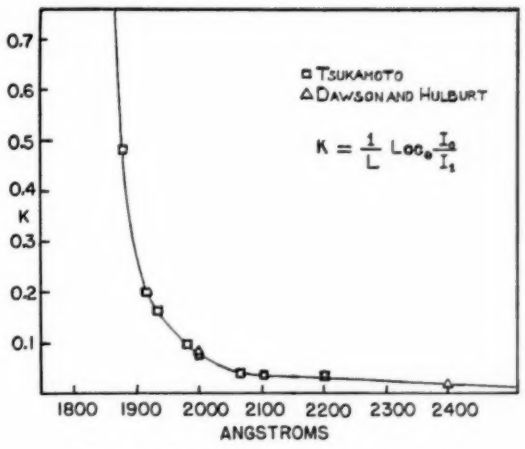

FIG. 5. Absorption spectrum of water.

in Fig. 5 is given a graph of the absorption coefficients of water in this region.[5, 6] For sulfate concentrations greater than 10 millimolar, the influence of 1860A is negligible. If we assume that the hydrogen produced at the higher sulfate concentrations is due to the aluminum lines at 1934A and 1990A, and that the same number of quanta are emitted by the spark at these two wave-lengths, a calculation shows that the quantum efficiency of the water-photosensitized reaction at 1990A is of the order of 1/10 of the quantum efficiency at 1934A. Below 1934A the quantum efficiency appears to be of the same order as that of the direct photodecomposition of the methyl alcohol. (Compare Fig. 2.) For methyl alcohol in the vapor phase, this quantum efficiency was found by Patat[2] to be of the order of unity.

At wave-lengths longer than shown in the graph of Fig. 5, the absorption of water decreases continuoously,[6] but over the whole spectrum remains much greater than one would expect, on theoretical grounds, from scattering. As determined by the action on methyl alcohol, the photochemical activity of water appears to stop in the neighborhood of 2000A. This does not necessarily mean that the photochemical activity of water has an absolute limit at this wave-length. Studies of the action on molecules other than methyl alcohol appear to show that

[5] K. Tsukamoto, Rev. d'optique **7**, 89 (1928).
[6] L. H. Dawson and E. O. Hulburt, J. Opt. Soc. Am. **24**, 175 (1934).

the photochemical activity extends still further out. Unfortunately, because of the low absorption of water at these long wave-lengths, the chemical effects are small and it is a matter of considerable difficulty to eliminate or correct for direct photodecomposition.

We have remarked that water is not decomposed under the conditions of irradiation used in the present experiments (Fig. 1). This is what one would expect, in view of the fact that no decomposition is obtained even upon irradiation with x-rays.[3e] Several investigators[7–11] have claimed decomposition occurs under conditions of irradiation which would appear to supply considerably less energy in the region below 2000A, than has been used in the present experiments. In some of these experiments the decomposition of organic and other impurities (compare above) in the irradiated water may have been misinterpreted as a decomposition of the water. One other possibility should also be kept in mind: Water may be decomposed in the presence of certain impurities acting catalytically. This has been found to be the case for x-rays. We recently reported[3h] that traces of the iodide or bromide ion were effective with x-rays in this respect. These particular ions, however, have no action in the case of light.

We wish to thank Mr. D. M. Gallagher for his assistance in this work.

[7] M. Kernbaum, Comptes rendus **149**, 273 (1909).
[8] Thiele, Zeits. f. angew. Chemie **22**, 2472 (1909).
[9] A. Coehn, Ber. chem. Ges. **43**, 880 (1910).
[10] D. Bertelot and H. Gaudechon, Comptes rendus **150**, 1690 (1910).
[11] Tian, Ann. de physique [9] **5**, 248 (1916).

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Spectroscopic Studies of the Simpler Porphyrins

I. The Absorption Spectra of Porphin, *ms*-Methyl Porphin, *ms*-Ethyl Porphin, *ms*-Propyl Porphin and *ms*-Phenyl Porphin*

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The molecular absorption coefficients of porphin and four *ms*-substituted porphins have been measured throughout the visible region and the curves showing absorption coefficient as a function of wave-length are shown. All of the substances have a very strong absorption band at the violet end of the visible region. The rest of the spectrum, while similar in pattern for all of the substances, shows some characteristic differences.

INTRODUCTION

IN previous papers,[1, 2] the fluorescence spectra and photodecomposition of the chlorophylls and some of their derivatives were discussed. It was found that the fluorescence spectra of all of the substances studied showed a similar pattern. Because of this, it seemed desirable to make similar studies on simpler chlorophyll derivatives. An ideal series of substances for this purpose is now available since Dr. Paul Rothemund,[3, 4] at this laboratory, has succeeded in synthesizing porphins from substances of aldehydic function and pyrrole. The formula for porphin, which is formed from pyrrole and formaldehyde, is shown in Fig. 1. This substance is of considerable interest, as it is the simplest form of the ring system of the two biologically important pigments, haemin and chlorophyll. It is apparent from Fig. 1 that two isomeric forms of this substance are possible, one with the

* This work was done with the experimental cooperation of Mr. Alex Horvath on a special scholarship arrangement.
[1] V. M. Albers and H. V. Knorr, Cold Spring Harbor Symposia on Quantitative Biology **3**, 87–97 (1935).
[2] Reference 1, pp. 98–107.
[3] Paul Rothemund, J. Am. Chem. Soc. **57**, 2010 (1935).
[4] Paul Rothemund, J. Am. Chem. Soc. **58**, 625–627 (1936).

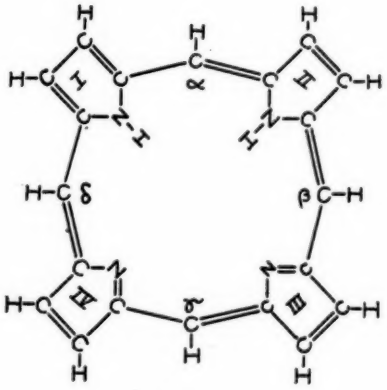

FIG. 1.

hydrogens linked to the nitrogen atoms in adjacent rings, as indicated, and one with the hydrogens linked to the nitrogen atoms in opposite rings with a corresponding rearrangement of the bonds in the ring. In this investigation the $\diagup\!\!\diagdown\!\!\diagup$N group has been tentatively assumed to be in rings I and II; further work will show whether this assumption is correct. The system of nomenclature, for these substances, suggested by Rothemund will be followed in this paper, i.e., *ms*-methyl porphin is the porphin with methyl groups substituted for H in the α, β, γ, and δ positions. A large number of these synthetic porphins as well as the corresponding phyllins and haemins are now available for study.

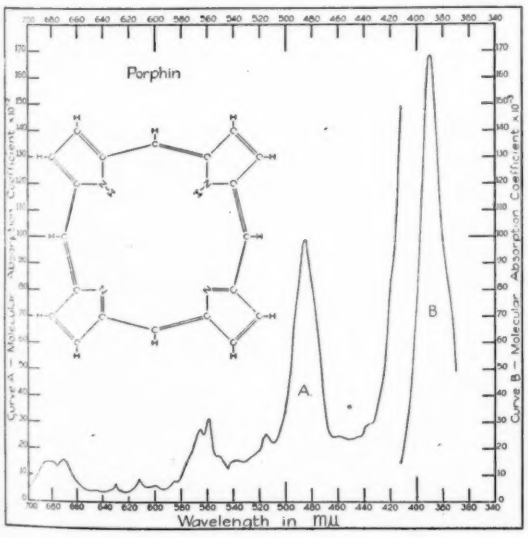

FIG. 2.

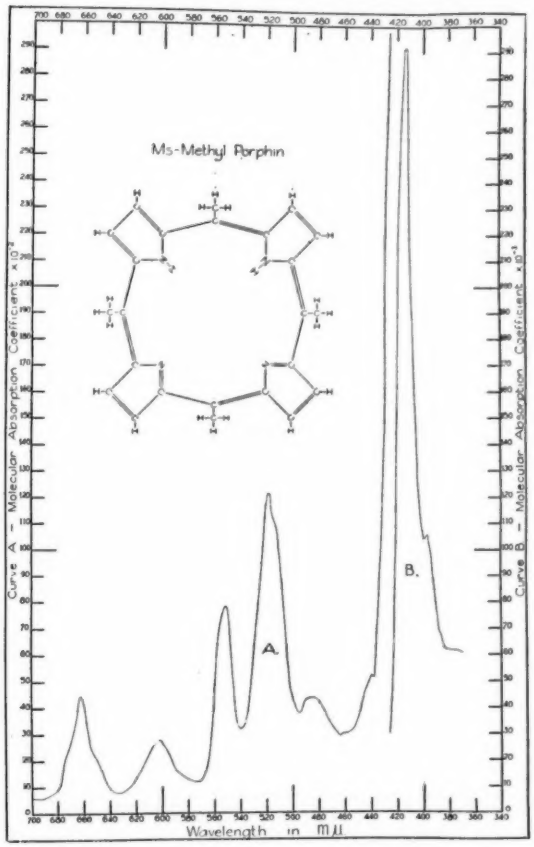

FIG. 3.

This paper will be concerned with measurements of the absorption coefficients throughout the visible region, of ether solutions of porphin, *ms*-methyl porphin, *ms*-ethyl porphin, *ms*-propyl porphin and *ms*-phenyl porphin.

EXPERIMENTAL

The transmissions of ether solutions of the substances were measured in the region from 370 mμ to 700 mμ. The source of continuous radiation was a "photoflood" lamp operated at 120 volts from a motor-generator set. A voltage regulator on the motor-generator set maintained a constant potential difference at the terminals of the lamp. The spectra were photographed with a Hilger E-3 spectrograph using Eastman I–L spectroscopic plates. Each plate was calibrated by making a series of exposures through neutral screens of known transmission, according to the method of Harrison.[5] In all

[5] George Harrison, J. Opt. Soc. Am. **19**, 267–316 (1929).

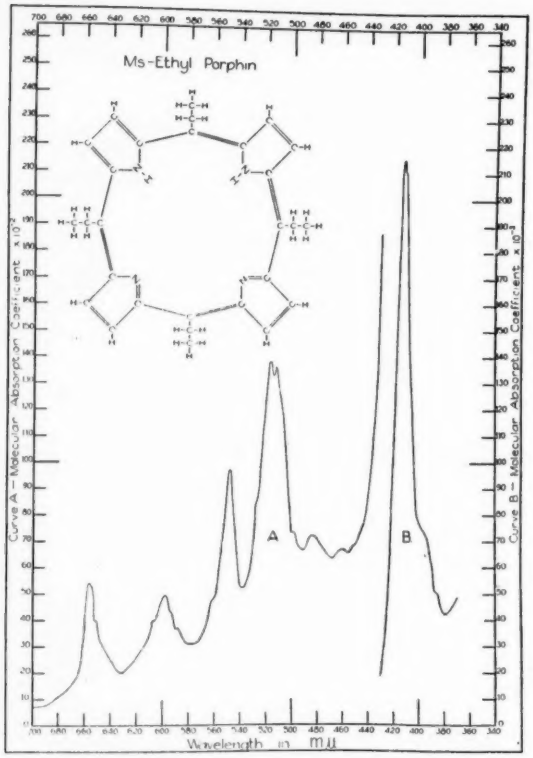

FIG. 4.

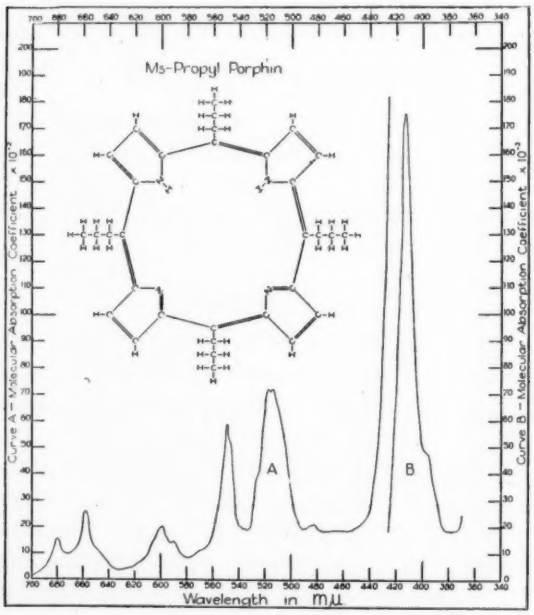

FIG. 5.

cases the exposure times for the calibration and absorption spectra were the same. Because of the great variation in the transmission of the

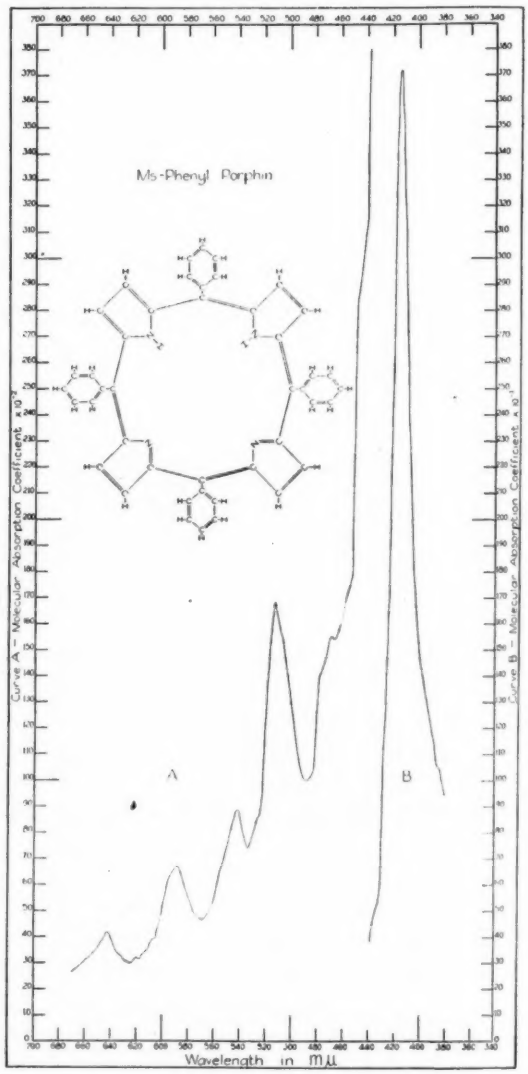

FIG. 6.

solutions, throughout the region investigated, a series of concentrations (in most cases seven) were used, with each successive concentration 50 percent of the one preceding it in the series.

Densitometer curves were obtained for all exposures on a plate, showing galvanometer deflections as a function of wave-length. A characteristic curve was determined for every 50A from the densitometer curves of the spectrograms which were made through the neutral screens. It was found, by trial, that a value of percent transmission for a solution, at a wave-length between those at which the characteristic curves were plotted, could be obtained by inter-

TABLE I.

	Wave-Length (mμ)	a		Wave-Length (mμ)	a		Wave-Length (mμ)	a
Porphin	390	168 ×10³	*ms*-methyl	413	292 ×10³	*ms*-propyl	413	175.5 ×10³
	485	9.83 "	porphin	485	4.35 "	porphin	483	2.10 "
	515	2.55 "		517	12.2 "		514	7.17 "
	559	3.20 "		551	7.80 "		518	7.17 "
	565	2.73 "		602	2.80 "		549	5.87 "
	585	0.78 "		662	4.45 "		590	1.45 "
	612	0.85 "					599	2.00 "
	630	0.67 "	*ms*-ethyl	413	215 ×10³		658	2.57 "
	671	1.57 "	porphin	460	6.70 "		680	1.55 "
	683	1.50 "		483	7.25 "			
				512	13.6 "	*ms*-phenyl	414	372 ×10³
				516	13.8 "	porphin	468	15.5 "
				547	9.70 "		512	16.8 "
				597	4.95 "		541	8.85 "
				656	5.40 "		588	6.70 "
							643	4.17 "

polation from the curves at 50A intervals within the limits of error of reading the curves. The absorption cell filled with pure ether was placed in the light path while the calibration exposures were being made. Therefore, 100 percent transmission represents the transmission of the absorption cell filled with pure ether. The length of the light path in the absorption cell was one cm. The 365-mμ line of Hg was used as a reference line on all exposures for wave-length determinations. The wave-lengths were then read from a previously determined dispersion curve for the spectrograph. With this arrangement, wave-lengths could be consistently read to within ±0.5 mμ at 580 mμ. These limits were established by measurements made on the 577 and 579 mμ lines of Hg.

For the measurements, the pure crystallized substances were dissolved in a small amount of pyridine and adjusted to a suitable concentration by addition of ether. The presence of the small amount of pyridine in the solution does not alter the spectrum from that of the pure ether solution.[6]

The absorption coefficients were calculated using Beer's law in the form of Eq. (1),

$$I_T/I_O = e^{-acx}, \qquad (1)$$

where I_T/I_O is the ratio of transmission of the absorption cell filled with the solution to the transmission of the cell filled with pure solvent, c is the concentration of the solution, measured in moles per liter, x is the thickness of the absorption cell in cm and a is the absorption coefficient of the substance.

[6] Kirstahler, Tab. Biol. Period. 1, 258 (1931).

Discussion of Results

Figs. 2 through 6 show the absorption coefficient curves for the substances, as well as their structural formulae. The outstanding characteristic of the spectra of these substances is a very strong band located in the violet region of the spectrum. This band occurs at 390 mμ in porphin, at 413 mμ in all of the aliphatic substituted meso-porphins, and at 414 mμ in the *ms*-phenyl porphin. It is interesting to note that the absorption coefficients for this band in the aliphatic substituted porphins are larger than the corresponding absorption coefficient for porphin, but that their value decreases as the length of the carbon chain increases. While the general pattern of the spectra in the longer wave-length region is similar for these substances, it is difficult to make direct comparison between corresponding bands. In Table I the wave-lengths and absorption coefficients of the principal bands of these substances are tabulated.

Beer's law apparently holds throughout the visible region for these substances since absorption coefficients for different solution concentrations at the same wave-length agree very well.

An Effect of Ultrasonic Radiation on Electrodeposits

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IT has been shown by Wood and Loomis[1] that ultrasonic radiations will produce ripples in a coating of warm paraffin on a glass tube placed with its lower end in the oil over a vibrating quartz plate. The authors have observed that similar ripples are produced in cathodic electrodeposits of several metals and alloys when plated under the conditions described below.

Sound waves having a frequency of about 1700 kilocycles were generated by a piezoelectric quartz crystal, 2.54 cm in diameter and 0.154 cm thick placed between brass electrodes and excited by a 250-watt oscillator. A 50-cc beaker containing the electrolyte was placed directly over the top electrode with a film of oil between the electrode and the ground glass bottom of the beaker. The cathode was placed directly over the center of the crystal between two electrodes, as shown in Fig. 1. Neither the cathode nor the anode touched the beaker.

Table I summarizes the results and gives the conditions under which the electrodeposits were formed. The electrodeposited brass mentioned in the table had a composition of about 30 percent Zn and 70 percent Cu, while the composition of the black nickel was about 65 percent Ni, 10 percent S, and 25 percent Zn. The alloys were tried in order to determine whether there would be any great difference in composition on the deposit in the thick part of a ripple as compared to that in the thin part. In the case of brass, if there should have been such a difference there would have been a difference in color of the deposits in the two places. No such difference was observed.

The velocity of the sound waves in the liquid, computed from measurements of the distance between ripples, taken as a half wave-length, corresponded approximately to that obtained by other methods.

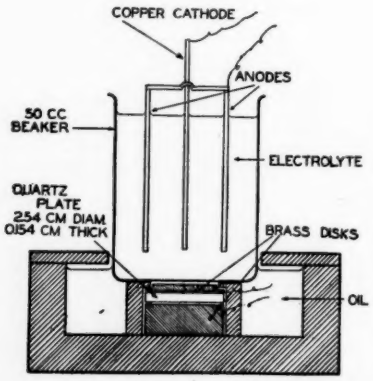

FIG. 1. Arrangement of the electrodes, beaker, and quartz piezoelectric crystal.

TABLE I

METAL	COMPOSITION OF THE BATH (grams per liter)		CURRENT DENSITY (amp./dm²)	TIME (minutes)	RESULTS
	Ferrous chloride	300			Very good ripples
Iron	Calcium chloride	150	5	60	See Fig. 2
	Ferrous sulphate	200			
Iron	Magnesium sulphate	100	5	60	Good ripples
	Ferrous sulphate	130			
	Ammonium chloride	100			
Iron	Sodium citrate	3	5	60	Fair ripples
	Cobalt ammonium sulphate	200	5	60	Poor ripples
Cobalt			5	15	Fair ripples
	Sodium cyanide	75			
	Cadmium oxide	25			
Cadmium	Sodium hydroxide	15	5	60	Poor ripples
	Chromic acid	250			No ripples. That deposited in the bath agitated by U.S. was not as bright as a control
	Sulphuric acid	3	4	60	
Chromium					
	Zinc sulphate	250			
	Ammonium chloride	15			
Zinc	Sodium acetate	15	4	30	Good ripples
	Zinc cyanide	30			Fair ripples. That deposited in the bath agitated by U.S. was not as bright as a control
	Sodium cyanide	30			
	Sodium hydroxide	25	4	30	
Zinc					
	Copper cyanide	30	4	30	No ripples
	Sodium cyanide	45			
	Zinc cyanide	7.5	1.5	30	No ripples
	Sodium carbonate	15			
Brass			0.5	30	Fair ripples
	Nickel ammonium sulphate	50			
	Ammonium sulphocyanate	50			
Black Nickel	Zinc sulphate	60	4	30	Good ripples

The temperature of all the plating baths was 47°C.

[1] R. W. Wood and Alfred L. Loomis, Phil. Mag. **4**, 417 (1927).

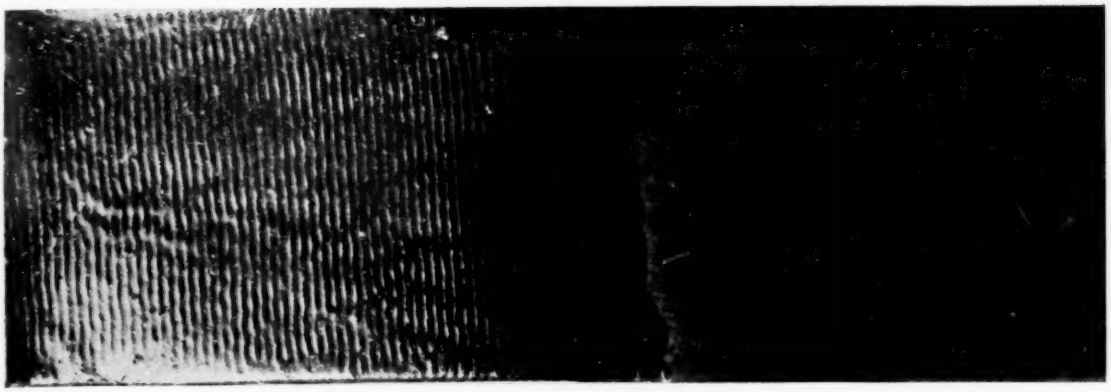

FIG. 2. Ripples in electrodeposited iron produced by ultrasonic radiation (enlarged).

The results seem to indicate that stationary waves are set up in the solution and that the metal ions are relatively more concentrated in layers which are separated by half wave-lengths. In the case of iron and zinc it appears from the results given in Table I that deposits showing the best ripples are obtained from the more concentrated solutions.

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The Dispersion of Sound in Oxygen

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The velocity of 1000-cycle sound wave in oxygen of various degrees of humidity at 26.5°C has been measured. The velocity behavior indicates that the water molecules are effective in bringing the heat capacity of the first vibrational state of the oxygen molecule into equilibrium with the sound wave. The dispersion change in velocity amounts to 0.16 percent. Intensity measurements agree with velocity data in fixing the center of the dispersion region between 1 and 3 mm partial pressure of water, which is in agreement with the values calculated from Knudsen's studies of rates of decay at higher frequencies.

THE classical work of Knudsen and Kneser[1, 2, 3] on the rates of decay of sound waves in mixtures of air and water vapor, and oxygen and water vapor, showed that there was an optimum humidity at which the rate of decay has a maximum value, and showed definitely that the effects observed were due to the efficiency of water molecules in activating the first vibrational state of the oxygen molecule and in returning this vibrational heat capacity to the sound wave. On the basis of the recently developed theory of sound dispersion[4, 5, 6] there should be an anomalous behavior in velocity accompanying the appearance of a maximum rate of decay. The velocity of sound in air and oxygen has been determined by several investigators.[7, 8, 9] Pierce originally reported that at audiofrequencies measurements in dry air and in air at 36 percent and 55 percent humidity indicated no change in velocity with change in humidity within an accuracy of 0.021 percent.

[1] Knudsen, J. Acous. Soc. Am. **5**, 112 (1933); **6**, 199 (1935).
[2] Kneser and Knudsen, Ann. d. Physik **21**, 682 (1935).
[3] Kneser, J. Acous. Soc. Am. **5**, 122 (1933).
[4] Einstein, Ber. d. Berlin Akad. S380 (1920).
[5] Herzfeld and Rice, Phys. Rev. **31**, 691 (1928).
[6] Kneser, Ann. d. Physik **11**, 777 (1931).
[7] Pierce, Proc. Am. Acad. **60**, 286 (1924).
[8] Reid, Phys. Rev. **35**, 814 (1930).
[9] Brass and Bastile, J. Math. Phys., M.I.T. **2**, 210 (1913).

Reid, working in Pierce's laboratory, later modified these results to show that the velocity of sound in air at 20°C was a linear function of the humidity. However, he measured the velocity only at 0, 45 and 100 percent relative humidity using supersonic frequencies.

If we accept Knudsen's data as fixing a dispersion at roughly 0.21 percent water molecules in air and 0.40 percent in oxygen for frequencies of the order of 3000 cycles, then the change in velocity should not be linear with humidity. As water molecules are added to dry oxygen or air, there should normally result an increase in velocity due to decrease in density, and for very small changes in density resulting from the addition of small quantities of water vapor this increase should appear almost linear, since the velocity of sound changes with density according to the familiar equation

$$v=[(p/d)\gamma]^{\frac{1}{2}},$$

where p is pressure, d density, and γ the ratio of specific heats. The change in velocity due to γ for water being less than γ for O_2 is small compared to the density effect. However, if the addition of water molecules serves to activate the first vibrational state of the oxygen molecules with sufficient rapidity so that the vibrational heat capacity is returned to the apparent heat capacity of the gas in the sound wave, then γ must decrease, and correspondingly the velocity must decrease. The density change and dispersion have therefore opposite effects in changing velocity. If, then, velocity is plotted against percent of water molecules present, the curve should have a different character in passing through the dispersion region than in the region where there is no dispersion and the change of velocity with density alone is operative. An apparatus was therefore constructed for measuring the change of velocity in a sound wave passing through oxygen containing various percentages of water vapor, in the hope of detecting the dispersion effect. Oxygen was selected rather than air because of the larger effect observed in the case of oxygen, since dispersion in air is due only to the oxygen molecules present.

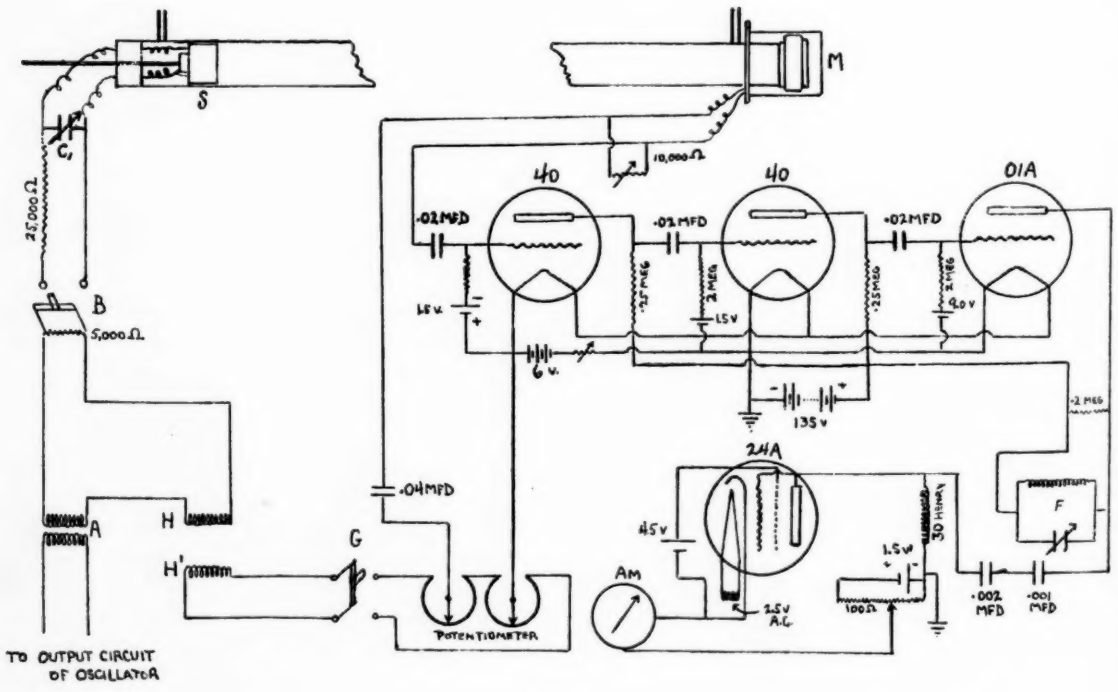

FIG. 1.

Apparatus

The apparatus shown in Fig. 1 consisted essentially of a resonance tube, with a microphone fixed at one end, and a movable speaker unit in the tube. The resonance cell was a Pyrex glass tube nine feet in length and with an inside diameter of 6.3 cm. Tubes sealed at each end of the cell led to a centrifugal pump and a circulation system whereby the oxygen could be circulated over P_2O_5 or through a glass spiral containing pockets filled with water. The cell was thermostated in a water bath, the temperature being held at $26.50 \pm 0.1°C$.

The speaker was an American Bell headphone unit held in a brass case, and with a heavy brass plate with a 9.5-mm hole in its center holding the diaphragm. The sender was attached to a long rod which extended out of the cell in a rubber tube, allowing the sender to be moved down the resonance tube.

The microphone, M, was a modified Baldwin speaker unit whose aluminum face had been turned out and a brass plate similar to the one used on the sender, was inserted. These two brass plates offered smooth parallel reflecting surfaces for the sound at each end of the cell. The microphone was mounted at the end of the tube and was enclosed in a glass case. All joints and electrical leads were sealed with a mixture of beeswax and rosin. All free space, except the resonance portion of the cell, was liberally padded with felt.

The oscillator used to actuate the sending unit consisted of an oscillating circuit controlled by a 1000-cycle tuning fork. A headphone unit without diaphragm was mounted close to each arm of the tuning fork. The one serving as a pick-up was connected to the input of a 60-decibel 5-watt amplifier. Part of the output of the amplifier passed through the other phone unit maintaining the vibration of the tuning fork. The output circuit was tuned until an excellent wave form was obtained.

The electrical measurement circuit is shown in Fig. 1. The capacity C across the speaker was adjusted until the speaker had a natural frequency of 1000 cycles, thus giving a sine sound wave free from harmonics. The wave form from the microphone was also excellent when the cell was set at resonance. The voltage generated in the microphone was amplified by a three-stage resistance coupled amplifier. The plate circuit of the last tube was tuned to 1000 cycles. The output then led to the vacuum tube voltmeter, V. This voltmeter gave very close to a linear response and was well suited for measuring the small AC output of the amplifier.

The electrical set-up, as described to this point, would have required calibration with known voltage inputs to the amplifier, and any subsequent changes in the amplifier or vacuum tube voltmeter characteristics, or change in the output of the oscillator due to long period 60-cycle a.c. voltage fluctuations, would have invalidated the calibration.

A method of eliminating the inaccuracy introduced by any of the above fluctuations, consisted in loosely coupling from the oscillator output by means of the two honeycomb coils H and H' and causing the induced current to flow through the battery terminals of a Leeds and Northrup Student Type potentiometer. The slide wire, or e.m.f., terminals of the potentiometer, were in series with the microphone and input to the amplifier. The procedure in taking readings consisted in opening the switch G and closing the switch B, and observing the swing of the milliammeter caused by the sound wave incident upon the microphone. Switch B was then opened and switch G closed and the potentiometer adjusted so that sufficient induced current from H' was thrown into the amplifier input to duplicate the swing of the milliammeter. As a check, the operation was repeated. The reading on the potentiometer then represented the relative intensity of the sound incident on the microphone. The effect of any variations in the system other than mechanical changes in the sender or microphone units were thus eliminated. However, intensity readings could only be taken between 1 and 5 A.M. when the power lines were free from rapid voltage fluctuations and "static."

In obtaining readings of the change in intensity and velocity with the addition of water vapor to oxygen, the following procedure was used. The resonance cell was first evacuated to 0.1 mm and flushed out several times with oxygen, and then filled to 733-mm pressure. The oxygen was

circulated through the cell and over P_2O_5 to insure its dryness. The sender was adjusted to resonance at seven and one-half wave-lengths from the microphone as indicated by the maximum swing on the milliammeter, and the intensity reading taken on the potentiometer. The position of the sender was noted by means of the position of the adjusting rod relative to a scale at the end of the tube. The oxygen was then circulated through the water spiral until the pressure of the system as registered on the manometer showed a small rise. The water spiral was then cut out of the system and the circulation continued to insure thorough mixing of the water vapor and oxygen. The resonance position and intensity were again determined. This process was repeated a number of times. Readings taken at one-half wave-length showed no appreciable change in end effect with varying humidity. There was only a negligible change in resonance position when the density of pure oxygen was decreased by reducing the pressure. This was not the case until felt padding was introduced to prevent extraneous resonances. Since the change in velocity was less than 0.3 percent, the change in the tube correction can be neglected.

Table I shows a sample series of determinations of the intensity at resonance at various humidities. The results are graphed in the upper curve in Fig. 2. Measurements made on different days give a minimum at the same partial pressure of water but the absolute intensities were not in good agreement. The intensity data merely fix the center of the dispersion between 1 and 3 mm partial pressure of water vapor. Table II shows the change in resonance position of the sender with different partial pressures of water vapor. The position with pure oxygen was 247 cm from the microphone. The relative velocity was calculated as (2470+displacement)/2470. In this way it was only necessary to know the absolute velocity in the tube to one part in 250 in order to get the relative velocity accurate to better than 1 part in 10,000. The lower curve in Fig. 2 shows the relative velocity plotted against the mm water vapor present in 733 mm of oxygen. The velocity decreases up to approximately 2 mm water vapor and then starts to increase in a normal manner due to the increase in the ratio of the pressure to the density. Extrapolating the straight-line portion of the curve beyond 4 mm to zero water vapor pressure, we find the relative velocity the sound would have in pure oxygen if the vibrational heat capacity had been present. This extrapolates to 0.9984 of the velocity in dry oxygen, a decrease of 0.16 percent.

Taking the vibrational heat capacity of oxygen at 26.5°C as 0.63 cal./mole/degree,[10] the percentage change in velocity due to dispersion should be 0.19 percent. The agreement is within the error in extrapolating the experimental data. This verifies Henry's[11] explanation of the sys-

Table I.

mm H_2O	0	1	3	6	10	14	18
Intensity	920	870	870	920	926	928	929

Table II.

mm H_2O	mm Displacement	Relative Velocity	mm H_2O	mm Displacement	Relative Velocity
0.	0.	1.00000	5.3	−.5	.99980
.7	−1.0	.99960	5.4	+.5	1.00020
1.0	−2.1	.99915	6.5	1.0	1.00040
1.1	−2.5	.99899	7.9	1.8	1.00073
2.3	−2.1	.99915	13.9	6.0	1.00243
2.5	−2.0	.99919	14.6	6.3	1.00255
3.7	− .6	.99976			

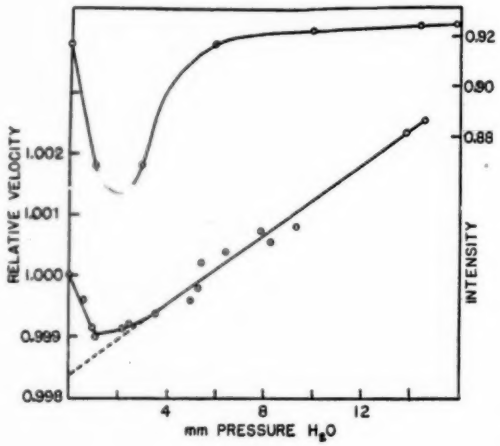

Fig. 2.

[10] Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

[11] Henry, Nature **129**, 200 (1932).

tematic error in the heat capacity of oxygen from velocity of sound measurements.[12, 13]

Comparison of the reported heat capacity[12, 13] of oxygen from velocity of sound measurements with the value obtained by other methods, shows that the former is too low by the heat capacity due to the first vibrational state up to about 1000°K. At 1400°K, where the second vibrational state should contribute an appreciable amount to the heat capacity, the difference is still greater. This indicates that neither the first or second vibrational levels are activated by the sound wave even at these temperatures.

Measurements of the relative velocity of sound are being continued at higher frequencies where the experimental error will be lower.

[12] Shilling and Partington, Phil. Mag. **6**, 920 (1928).
[13] King and Partington, Phil. Mag. **9**, 1020 (1930).

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Dielectric Constants of Extremely Dilute Solutions

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(Received March 27, 1936)

The dielectric behavior of unusually dilute solutions of ethyl alcohol in the nonpolar solvents benzol and carbon tetrachloride have been investigated down to 0.00007 mole-fraction concentration of alcohol. This concentration of molecules corresponds to a gaseous pressure of only 1.5 cm of Hg. The effect of an apparently anomalous behavior often present in the usual method of treating data has been eliminated by a slightly different treatment. Effects of association are entirely absent up to concentrations nearing 0.01. Molecular polarizations of alcohol at 24.5°C, evaluated by least squares from data using the two solvents, agree closely; they also agree well with accepted vapor data. Taking over the molecular refraction of alcohol from optical data, the electric moment of the ethyl alcohol molecule is found to be $(1.700\pm0.006)\times10^{-18}$ from benzol solution and $(1.674\pm0.005)\times10^{-18}$ from carbon tetrachloride solution. These are felt to be unusually reliable for solution values; they compare favorably indeed with the two best vapor values, 1.696×10^{-18} by Miles and 1.686×10^{-18} by Knowles. Accurate density-concentration relationships for very dilute alcoholic solutions are given.

MANY writers have investigated the behavior of polar liquids in nonpolar solvents by way of determining the electric moment of the dissolved molecule. The usual procedure[1] is to assume that the molecular polarization of the solution P_{12} is the sum of the contributions of the solvent and the solute; thus

$$P_{12}=P_1c_1+P_2c_2,$$

where P_1 and c_1, and P_2 and c_2 are the molecular polarizations and the mole-fraction concentrations of the solvent and the solute, respectively. Calculations of P_2 from observed values of P_{12} at various concentrations, using a fixed value of P_1 observed for the pure solvent, show that the molecular polarization P_2 of the polar solute varies in general with concentration. This variation is attributed to association. It is customary to plot values of P_2 *versus* the solute concentration c_2, and extrapolate this curve to zero concentration. It is assumed that the solute polarization so obtained is free from effects of association. That this is essentially true is evidenced by the fact that electric moments calculated in this way for many molecules agree fairly well with moments obtained from vapor studies. Nevertheless one is impressed by the fact that, to the best of the author's knowledge, no worker has obtained data on sufficiently dilute solutions and at the same time of sufficient accuracy to show that the solute polarization P_2 actually does become constant at some low concentration, thus indicating complete lack of association effects. In fact in certain instances where investigators were forced by sparing solubility of the solute to use extremely dilute solutions, apparently anomalous results were

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[1] See, for example, Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, 1931).

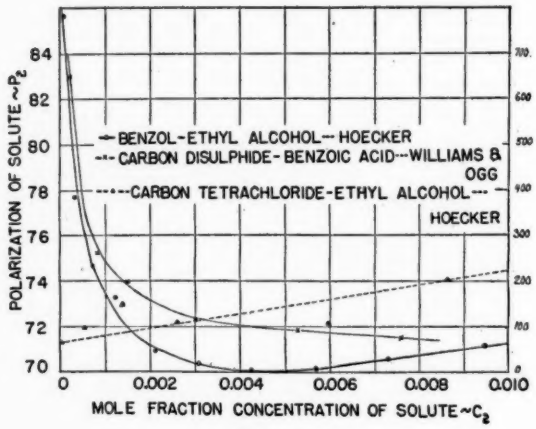

FIG. 1.

obtained. This is indicated by the curve through the cross-points of Fig. 1, plotted by the author from data by Williams and Ogg.[2] The writer obtained similar results in some early measurements on ethyl alcohol in extremely dilute benzol solution; these are shown by circle points in the same figure. Such behavior precludes any possibility of proper extrapolation to zero concentration.

Recently, Müller and Mortier[3] have observed similar effects on several alcohols (not including ethyl alcohol) using various solvents. They state that such an effect will always be observed whenever sufficiently precise measurements are made on extremely dilute solutions of polar solute in nonpolar solvent, and interpret the effect as the result of the varying effect of the solvent upon the association mechanism of the solute.

The present work was undertaken with the hope of obtaining accurate data on extremely dilute solutions to see whether the solute polarization actually does become constant at low concentration and remain at this fixed value for all lower concentrations. If such is possible, one would presumably be able to obtain a much more reliable value of zero concentration intercept than is usually obtained by extrapolation from a region where association effects are still present. The polar liquid studied was ethyl alcohol. This was dried by refluxing over CaO and later distilling over sodium. The nonpolar liquids used were benzol, carbon tetrachloride, and carbon disulfide. Every precaution was taken to obtain liquids of high purity.

The heterodyne beat apparatus used for dielectric constant measurements was designed to insure precision measurements of extremely small capacity changes. In its ultimate form it was essentially that described by Stranathan,[4] except that it was not a.c. operated. The critical oscillator was stabilized as suggested by Llewellyn,[5] and was inclosed in a constant-temperature water bath which contained also the test condenser. The standard precision condenser described by Stranathan[6] was used to measure the small increases in capacity caused by addition of small quantities of the solute. Capacity changes as small as $0.006\mu\mu f$ could be measured. The test condenser and mixing reservoir were constructed of brass; Pyrex was used for insulation in the condenser. This condenser was mounted permanently in the constant-temperature bath and arranged so that the mixing reservoir could be attached to transfer a solution without exposing the solution to the air. This reduced evaporation effects materially. A method of successive dilutions was used in mixing solutions.

Because of the precision required in these measurements, it was necessary to make accurate determinations of the variation of density of the solution with concentration of alcohol. A special type of pycnometer described by Parker and Parker[7] was used. It is believed these density-concentration relationships are the most precise available on these solutions. Measurements made on solutions of various mole-fraction concentrations ranging from 0.0004 to 0.10, all at 24.5°C, show that the change in density due to addition of alcohol is strictly linear. A least-squares solution involving measurements at fifteen concentrations shows that the density of a benzene-ethyl alcohol solution is given by

$$d=(0.87197\pm0.000055)-(0.06717\pm0.00048)C_2.$$

From measurements on nine solutions of ethyl alcohol in carbon tetrachloride

$$d=(1.585547\pm0.0000013)-(0.51191\pm0.00017)C_2.$$

[2] Williams and Ogg, J. Am. Chem. Soc. **50**, 94 (1928).
[3] Müller and Mortier, Physik. Zeits. **36**, 375 (1935).
[4] Stranathan, Rev. Sci. Inst. **5**, 334 (1934).
[5] Llewellyn, Proc. I. R. E. **19**, 12 (1931).
[6] Stranathan, Rev. Sci. Inst. **5**, 315 (1934).
[7] Parker and Parker, J. Phys. Chem. **29**, 132 (1925).

From measurements on nineteen solutions of ethyl alcohol in carbon disulfide

Undried $d=(1.25601\pm0.00018)-(0.49787\pm0.00347)C_2$,

Dried $d=(1.2561096\pm0.0000078)-(0.51548\pm0.00107)C_2$.

In the above statements the probable errors do not include any differences which might arise because of the purity of the solvent itself.

The dielectric polarization has been measured for fifty-seven solutions ranging from 0.00007 to 0.15 mole-fraction concentration of ethyl alcohol in benzene; forty-one of these solutions were under 0.01 concentration. Similar measurements have been made on forty solutions of ethyl alcohol in carbon tetrachloride, ranging from 0.00007 to 0.02 in concentration of alcohol. Thirty-four solutions of ethyl alcohol in carbon disulfide have been studied, all under 0.03 concentration. When the data from benzene solution are plotted in the usual manner, P_2 *versus* c_2, the anomalous behavior shown by the curve through circles in Fig. 1 is apparent at low concentrations. An extremely small error in the measurement of the molecular polarization P_1 of the pure solvent could cause this behavior; or the presence of small quantities of alcohol may actually increase slightly the polarization of the solvent benzene. At any rate it is hopeless to try to obtain a zero concentration intercept. The author has therefore chosen to treat the data in a manner entirely equivalent to that used in vapor studies. In such studies one obtains the molecular polarization of the vapor dielectric at a particular temperature from the slope of the linear curve of $(K-1)/(K+2)$ *versus* the ideal gas pressure p'. Since P_2c_2 is proportional to $(K-1)/(K+2)$, and since c_2 is a function of p', the author has plotted P_2c_2 *versus* c_2 in Fig. 2. The slope of this curve at any concentration gives the molecular polarization of the solvent at that concentration. The resultant curve is actually linear for both benzene and carbon tetrachloride solutions up to concentrations of 0.01 of alcohol. The polarization of alcohol is therefore constant over this extreme range of concentration from 0.00007 to 0.01; no measurable association effects exist within this range. To the best of the author's knowledge, this has never been demonstrated before. Data above 0.01 concentration have not been plotted, for in this vicinity association effects become apparent in each case. In benzene solutions association causes a slow but definite increase in the molecular polarization of alcohol; the curve becomes concave upward. In the case of carbon tetrachloride solutions, observations were not extended sufficiently above one percent to make certain of any association effect; it appears likely however that association starts appreciably between one and two percent concentration.

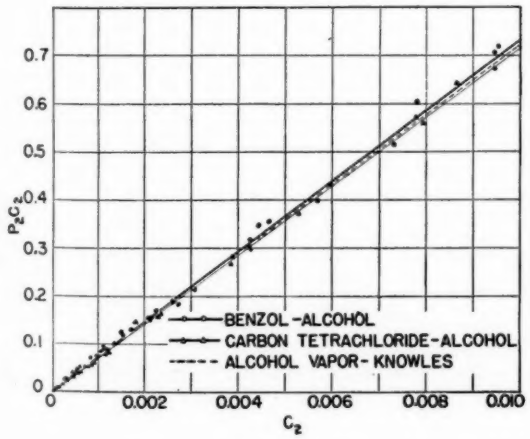

FIG. 2.

Observations made on ethyl alcohol, carbon disulfide solutions, which, when plotted in the above manner yield a rather irregular curve starting from zero concentration with essentially the same slope as that of the two curves shown but with slight downward concavity, are not shown here because there was some evidence of a very slight chemical action between the brass of the test condenser and the solution when carbon disulfide was used. The obvious alternative interpretation of this behavior, that association is not completely absent even at these low concentrations in carbon disulfide, seems hardly reasonable, since it is unlikely that alcohol molecules associate at these low concentrations when in carbon disulfide and do not when in carbon tetrachloride or benzol.

Since association effects are entirely absent over the wide range of concentration from 0.00007 to 0.01 shown in Fig. 2, the slope of the resultant line should give a reliable value for the

molecular polarization of ethyl alcohol at this temperature. A least-squares solution for the slope of this curve for ethyl alcohol-benzene solutions gives

$$\text{Slope} = P_2 = 73.16 \pm 0.42.$$

$$\text{Intercept on the } P_2C_2 \text{ axis} = 0.0034 \pm 0.0016.$$

A similar solution for ethyl alcohol carbon tetrachloride solution gives

$$\text{Slope} = P_2 = 71.31 \pm 0.33.$$

$$\text{Intercept on the } P_2C_2 \text{ axis} = 0.00002 \pm 0.001.$$

These two polarizations are seen to agree rather well. Knowles[8] has published data on ethyl alcohol vapor at 24.55°C obtained from measurements on twenty-eight different pressures of alcohol ranging from 0.2 to 6 cm of Hg. For comparison purposes his curve has been extended with the slope he specified and is shown dashed in Fig. 2. At this temperature he obtains a molecular polarization of 72.8. The author's values fall on either side of this. The author's data shown in the same figure covers a range of equivalent pressures from 1.5 to 200 cm of Hg. Thus the author's and Knowles' data overlap considerably, and the agreement between vapor and dilute solution data is rather remarkable.

The small intercept specified above for the ethyl alcohol-benzene curve, whether it be real or accidental, is consistent with the anomalous behavior apparent when data are plotted in the usual manner as in Fig. 1. The curve for ethyl alcohol-carbon tetrachloride solutions yields no intercept; and the data yield a fairly well defined intercept when plotted similar to Fig. 1. The author certainly would not claim that the intercept of the ethyl alcohol benzol curve is real, although Müller and Mortier[3] certainly consider the analogous effect observed by them on other substances to be so, and subgroups taken under quite different conditions seem to show the peculiar behavior rather consistently. One can appreciate how small an error is necessary to cause erratic behavior at extremely low concentrations only after making calculations involving such measurements. In fact considerable published data on vapors show analogous erratic behaviors at low pressures if the data are treated as one commonly treats solutions. The author wishes to emphasize that he has in no way eliminated this peculiar behavior at low concentrations but he has suggested a method of treating it so that the inaccuracies necessarily introduced do not appreciably effect calculation of the molecular polarization.

The electric moment of the alcohol molecule may be calculated from the polarization found above, along with the molecular refraction taken over from optical data. The electric moment is given by

$$u = 1.272 \times 10^{-20}((P_0 - A)T)^{\frac{1}{2}},$$

where P_0 is the molecular polarization when freed from association and where A is the polarization due to other than molecular doublets. Taking A as 12.9 as calculated from the index of refraction one calculates the moment of the ethyl alcohol molecule to be

$u = (1.700 \pm 0.006) \times 10^{-18}$ from benzene solution

and $u = (1.674 \pm 0.005) \times 10^{-18}$ from carbon tetrachloride solution.

These values compare favorably with each other and agree unusually well with two reliable values obtained from vapor studies, 1.696×10^{-18} by Miles,[9] and 1.686×10^{-18} by Knowles.[8]

Certain writers[10] have maintained that moments evaluated from benzene solution data must be multiplied by a certain factor greater than one in order to agree with moments obtained from vapor studies. The present findings are quite contrary to this. The agreement of moments here found is in all cases consistent with the probable errors; and actually the most probable value found from benzene solution is the highest of the group.

In conclusion the writer wishes to express his gratitude to Professor J. D. Stranathan for his continued interest in the progress of this work.

[8] Knowles, J. Phys. Chem. **36**, 2554 (1932).

[9] Miles, Phys. Rev. **34**, 964 (1929).

[10] See, for example, Müller (quoted), Chem. Soc. J. 1846–49 (1934).

The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

IV. Ethylene, Propylene, 1-Butene, *Cis* and *Trans* 2-Butene, Isobutene, Trimethylethylene, Tetramethylethylene and Butadiene

V. Equilibrium Constants for Reactions of Paraffins, Olefins and Hydrogen[1]

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(Received April 25, 1936)

IV. Methods previously developed by Eidinoff and Aston and by the writer are used to calculate the limiting high temperature rotational partition function and hence the translation-rotation entropy for the substances named in the title. The results are compared with third law values wherever possible. The agreement is fairly good in most cases, but the calculated values probably yield more accurate structural entropy differences. V. A consistent set of frequencies for methane, ethane, propane and butane is selected, and the corresponding vibrational contributions to $-F/T$ and H/T are tabulated. Equilibrium constants for the dehydrogenation reactions of ethane, propane, normal and isobutane are calculated and compared with experimental values. Systematic deviations are found which would be removed if the experimental equilibrium constants were reduced by a factor of 3, if the experimental hydrogenation heats were reduced by 1500 cal., or if the vibrational contribution to $-F/T$ at reaction temperatures were 2.5 cal./deg. greater for an olefin (excluding the torsional frequency) than for the corresponding paraffin. Approximate equilibrium constants are calculated for the reactions $2C_2H_4=C_4H_8$, $CH_4+C_2H_4=C_3H_8$, $CH_4+C_3H_6=C_4H_{10}$ and $C_2H_6+C_2H_4=C_4H_{10}$.

IV. Ethylene, Propylene, 1-Butene, *Cis* and *Trans* 2-Butenes, Isobutene, Trimethylethylene, Tetramethylethylene and Butadiene

THE method used here to calculate the limiting high temperature rotational partition function of nonrigid molecules has been described in a previous paper.[3] It is sufficient to repeat here that the calculations are based on a model in which all bond distances and bond angles are constant, the lack of rigidity being due only to rotations about single bonds. It is assumed that there is no potential energy associated with these rotations.

As was pointed out in the preceding article, the methyl derivatives of ethylene belong to the class of pseudo-rigid molecules and may be treated by the simplified method developed for that class. The C−C distance is taken as 1.53×10^{-8} cm, C=C as 1.36×10^{-8} cm, C−H as 1.11×10^{-8} cm. It is assumed that the angle between the two single bonds of an ethylene carbon atom is the normal tetrahedral angle, $\cos^{-1}(-\frac{1}{3})$. The reduced moments and translation-rotation entropies are given in Table I.

TABLE I. *Reduced moments and translation-rotation entropies of ethylene derivatives.*

SUBSTANCE	REDUCED MOMENTS $\times10^{40}$			S_{t+r}	$S_{t+r,\,298}$
Ethylene	35.380	29.916	5.464	$6.634+4R\log T$	51.915
Propylene	106.67	92.780	13.890	$11.725+9R/2\log T$	62.666
Cis 2-Butene	204.94	154.22	50.719	$11.624+5R\log T$	68.225
Trans 2-butene	246.41	231.19	15.217	$11.013+5R\log T$	67.614
Isobutene	185.19	93.004	92.185	$11.614+5R\log T$	68.215
Trimethylethylene	331.39	238.47	92.918	$13.158+11R/2\log T$	75.419
Tetramethylethylene	457.43	278.53	178.91	$10.050+6R\log T$	77.971

The calculation for the completely nonrigid molecule 1-butene is of course very much more difficult, but quite straightforward. The XY plane is taken parallel to the plane of the parent ethylene molecule, and the X axis parallel to the central C−C bond. The angle α measures the rotation of the C_2H_5 group, $\alpha=0$ being the position in which all four carbon atoms are in a plane, with the two end atoms on the same side of the two central ones. The angle β measures the rotation of the terminal methyl group. The masses of C and H are M and m; the C−C, C=C and C−H distances are D, D' and d.

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[2] Physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Kassel, J. Chem. Phys. **4**, 276–282 (1936).

The usual parameter μ associated with the differing centers of gravity for carbon and hydrogen is in this case

$$\mu = m/(6M+12m).$$

It is convenient to define a set of secondary parameters

$$P=(2/3+8\mu^2)MD^2, \quad Q=(1/2+8\mu^2)MD^2,$$
$$R=(3^{\frac{1}{2}}/36)MDD', \quad T=(1/4)MD'^2,$$
$$p=(16/9-8\mu/3+16\mu^2)mD^2, \quad q=(23/18-8\mu/3+16\mu^2)mD^2,$$
$$r=(3^{\frac{1}{2}}/6)mDD', \quad s=(4/9)mDd,$$
$$t=(1/2)mD'^2, \quad u=(4/9)3^{\frac{1}{2}}mD'd,$$
$$v=(4/9)md^2,$$

and a further set of tertiary parameters

$$A=P+p+4s+22v/3,$$
$$B=4R+2r,$$
$$C=Q+q+2R+r+s+v/3,$$
$$D=2T+2t+2u+4v,$$
$$E=7R+3r+T+t+u-v,$$
$$F=7P/2+2p-Q/2+q+14R+6r+9s+T+t+u+8v,$$
$$G=P+p+4s+4v/3.$$

It is then found that

$$K_{\alpha\alpha}=A+2v/3, \quad D_\alpha=A+2v/3-B\cos\alpha,$$
$$K_{\alpha\beta}=2v, \quad D_\beta=2v,$$
$$K_{\beta\beta}=6v,$$
$$E_\alpha=2^{\frac{1}{2}}(C-4v/3)\cos\alpha,$$
$$E_\beta=-4\cdot 2^{\frac{1}{2}}v\cos\alpha,$$
$$F_\alpha=-2^{\frac{1}{2}}(C-4v/3)\sin\alpha,$$
$$F_\beta=4\cdot 2^{\frac{1}{2}}v\sin\alpha,$$
$$\{xx\}+\{yy\}=D+F-2B\cos\alpha-(G-16v/3)\sin^2\alpha,$$
$$\{xx\}+\{zz\}=F-(G-16v/3)\cos^2\alpha,$$
$$\{yy\}+\{zz\}=A+2v/3+D-2B\cos\alpha,$$
$$\{xy\}=2^{\frac{1}{2}}[E-(C-4v/3)\cos\alpha],$$
$$\{xz\}=2^{\frac{1}{2}}(C-4v/3)\sin\alpha,$$
$$\{yz\}=(G-16v/3)\sin\alpha\cos\alpha-B\sin\alpha.$$

These are the elements of the determinant in (9) of Part I[3]; by obvious additions and subtractions of rows and columns this determinant is readily reduced from five rows to four. In this process the apparently inept definitions of A, C and G justify themselves, since the four-rowed determinant does not contain v explicitly. The complete expansion of the determinant is

$$|\mathfrak{D}|=6v\{ADF(D+F-G)-2AE^2(D+F)-2C^2DF$$
$$+\cos\alpha[4ABE^2-2ABD(F-G)+4BC(CD-BE)]$$
$$+\cos^2\alpha[-AD^2G+4BCE(D+F)-B^2F(D+F-G)-2C^2D^2]$$
$$+\cos^3\alpha[-4B^2CE+2B^2(F-G)]+B^2DG\cos^4\alpha$$
$$+\sin^2\alpha[-AB^2D+2AE^2G+4C^2E^2]+B^4\sin^2\alpha\cos^2\alpha\}.$$

Since this is a function of α there are no reduced moments. The integral of $|\mathfrak{D}|^{\frac{1}{2}}$ must be made by quadratures. It is found that the translation-rotation entropy is

$$S_{t+r}=15.873+5R\log T,$$
$$S_{t+r,\ 298}=72.474.$$

This value is about 0.5 e.u. lower than the estimate included in a preliminary report on this work;[4] the difference has been definitely traced to errors in making the estimate which it would be useless to discuss here. The translation-rotation entropy of 1-butene is thus about 4.5 e.u. higher than that of the 2-butenes. Only 1.4 e.u. of this difference is due to the fortuitous higher symmetry of the 2-butenes. The remaining 3.1 e.u. has its origin in the fact that 1-butene is formed from butane with the loss of only a low moment methyl-group rotation, while the rotation frozen out in 2-butene has a much higher moment. This difference may be expected to persist for higher olefins. There should be a further, somewhat smaller, decrease for these longer chain olefins as the double bond moves farther toward the center of the molecule.

Before solving the butadiene problem, it is convenient to develop from the general theory the special case of two rigid groups rotating about a common axis. We take this common axis to be the X axis and choose Y, Z axes so that the two groups rotate in opposite directions with equal angular speeds, and so that the center of gravity is in the YZ plane. Then the instantaneous positions of the atoms are

$$x_{i\alpha}=x_i,$$
$$y_{i\alpha}=y_i\cos\alpha+\delta_i z_i\sin\alpha,$$
$$z_{i\alpha}=\delta_i y_i\sin\alpha+z_i\cos\alpha,$$

where $\delta_i=1$ for atoms of one group and -1 for those of the other group, and α measures the rotation of either group with respect to some fixed axis in the YZ plane. Since the rotating groups are rigid, the x_i, y_i, z_i are constants. It

[4] L. S. Kassel, J. Chem. Phys. **4**, 144 (1936).

is now necessary to define another large group of new parameters.

$$\begin{array}{lll} \Sigma m_i = M, & \Sigma m_i y_i = aM, & \Sigma m_i \delta_i y_i = bM, \\ \Sigma m_i \delta_i z_i = cM, & \Sigma m_i z_i = dM, & \Sigma m_i x_i^2 = e, \\ \Sigma m_i x_i y_i = f, & \Sigma m_i \delta_i x_i y_i = g, & \Sigma m_i x_i z_i = h, \\ \Sigma m_i \delta_i x_i z_i = n, & \Sigma m_i y_i^2 = p, & \Sigma m_i \delta_i y_i^2 = q, \\ \Sigma m_i y_i z_i = r, & \Sigma m_i \delta_i y_i z_i = s, & \Sigma m_i z_i^2 = t, \\ & \Sigma m_i \delta_i z_i^2 = u. & \end{array}$$

The elements of the determinant are then found to be

$$K = p + t - M[(a \sin\alpha - c\cos\alpha)^2 + (d\sin\alpha + b\cos\alpha)^2],$$

$$D = -(q+u) + M(ab+cd),$$
$$E = g\cos\alpha - h\sin\alpha,$$
$$F = n\cos\alpha + f\sin\alpha,$$

$$\{yy\} + \{zz\} = (p+t) - M[(a\cos\alpha - c\sin\alpha)^2 + (d\cos\alpha + b\sin\alpha)^2],$$

$$\{xx\} + \{zz\} = e + (p - b^2M)\sin^2\alpha + 2(s - bdM)\sin\alpha\cos\alpha + (t - d^2M)\cos^2\alpha,$$

$$\{xx\} + \{yy\} = e + (p - a^2M)\cos^2\alpha - 2(s - acM)\sin\alpha\cos\alpha + (t - c^2M)\sin^2\alpha,$$

$$\{xy\} = f\cos\alpha - n\sin\alpha,$$
$$\{xz\} = g\sin\alpha + h\cos\alpha,$$
$$\{yz\} = (r - adM)\cos^2\alpha + (q - u - abM + cdM)\sin\alpha\cos\alpha - (r - bcM)\sin^2\alpha.$$

It is always possible to make $r=s=0$ by proper choice of the Y, Z axes, but it may not always be convenient to do so.

When the rotating groups have the X axis for one principal axis and have their other two principal axes parallel to the Y, Z axes when $\alpha=0$, this case reduces to one solved by Eidinoff and Aston.[5] Here

$$a=b=c=d=f=g=h=n=r=s=0$$

and the determinant reduces to

$$\{(p+t)^2 - (q+u)^2\}\{(e+p)(e+t) + (1/4)\sin^2 2\alpha[(p-t)^2 - (q-u)^2]\},$$

which is Eidinoff and Aston's result in a considerably changed notation. When the rotating groups are identical plane structures, as in butadiene,

$$b=c=d=f=h=n=q=r=s=t=u=0$$

and the determinant reduces to

$$\begin{vmatrix} p - a^2M\sin^2\alpha & g\cos\alpha \\ g\cos\alpha & e + p\sin^2\alpha \end{vmatrix} \times \begin{vmatrix} p - a^2M\cos^2\alpha & -g\sin\alpha \\ -g\sin\alpha & e + (p - a^2M)\cos^2\alpha \end{vmatrix}.$$

It is then readily found that for butadiene

$$S_{t+r} = 15.883 + (9R/2)\log T,$$
$$S_{t+r,\,298} = 66.824.$$

It is interesting to note that the entropy of 1-butene might have been estimated very accurately from the values for butane and butadiene. The butane value is $S_{t+r}=13.105+(11R/2)\log T$. The value for 1-butene should be $R\log 2 = 1.377$ higher than the mean of butane and butadiene, on account of the lower symmetry. Hence the predicted first approximation is $S_{t+r}=15.871+5R\log T$, only 0.002 lower than that directly calculated. The sign of this difference is that to be expected; expressed in another way, successive additions of hydrogen to butadiene would give entropy increases at 25°C of 4.273 and 4.269 e.u. if the symmetry number varied smoothly. The same trend appears more prominently when methyl groups are substituted successively in the 1, 3 and 5 positions of benzene. The symmetry-free entropy increases are then 5.39, 5.20, 5.02 e.u.

The various possible comparisons with third-law entropies are summarized in Table II. Wherever the boiling point is below 298°, comparisons at the boiling point also are shown;

TABLE II. *Comparison of calculated and observed entropies.*

	Entropies at 298.1°		Boiling point	Entropies at b. p.	
	S_{t+r}	S_{obs}		S_{t+r}	S_{obs}
Propylene	62.67	63.1	225.3°	60.16	59.2
1-Butene	72.47	(72.5)			
Cis 2-Butene	68.22	73.0	276.8	67.49	71.5
Trans 2-Butene	67.61	71.2	274.1	66.78	69.5
Isobutene	68.21	69.0	266.0	67.08	66.7
Trimethylethylene	75.14	(79.7)			

The experimental values for propylene are taken from Huffman, Parks and Barmore, J. Am. Chem. Soc. **53**, 3876–3888 (1931), and those for the butenes from Todd and Parks, J. Am. Chem. Soc. **58**, 134–137 (1936); 1-butene could not be crystallized and the value of S_{obs} for it is an estimate made by Todd and Parks. The value for trimethylethylene is obtained by combining the third-law entropy for the liquid determined by Parks and Huffman, J. Am. Chem. Soc. **52** 4381–4391 (1930), with an estimate of 20.2 e.u. for the entropy of vaporization given by Halford, J. Chem. Phys. **2**, 694–696 (1934).

[5] Eidinoff and Aston, J. Chem. Phys. **3**, 379–383 (1935).

TABLE III. *Relative frequencies of various molecular shapes.*

α	BUTADIENE	1-BUTENE	BUTANE	BUTANE, CORRECTED
0°	0.8980	0.8725	0.8425	0.8910
15	.9396	.9243	.9058	.9327
30	1.0207	1.0239	1.0268	1.0098
45	1.0671	1.0812	1.0966	1.0490
60	1.0482	1.0598	1.0731	1.0506
75	0.9935	0.9947	0.9978	1.0150
90	.9644	.9597	.9569	0.9940

at these lower temperatures the vibrational contribution is less, and better agreement might be expected. The differences between calculated and observed values for the 2-butenes are of the right order of magnitude to be overcome by the vibrational contributions omitted from the calculated values. The difference between the experimental values for the two isomers, however, is almost certainly too large. The agreement in the case of trimethylethylene is as good as could be expected when account is taken of the rough estimate used for S_{vap}. For propylene and isobutene the experimental values seem to be definitely too low; the estimate for 1-butene is also low. Aside from uncertainties in S_{vap}, the principal source of experimental error is probably in the long extrapolation from 90° to 0°K, which contributes 10 to 12 e.u.

These calculations also have bearing on the problem of the average shape of nonrigid molecules, since the integrands of the integrals leading to the partition function are proportional to the probability of finding a molecule with the corresponding angles. Table III contains normalized values of these integrands. The angle α in this table is that used for the butane and butadiene calculations and is equivalent to $\alpha/2$ of the 1-butene calculation. That is, $\alpha=0$ corresponds to the *cis* form of the carbon skeleton and $\alpha=90°$ to the *trans* form. It has been shown previously[6] that the dependence of vibrational frequencies on α produces a small pseudopotential energy opposing free rotation. For butane the maximum value of this potential for the lowest vibrational state was estimated as 59 cal. The values in the last column of Table III were obtained by multiplying those of the preceding column by $e^{-E(\alpha)/298k}$ and renormalizing, where $E(\alpha)$ is the estimated pseudopotential energy. This procedure, of course, cannot be exactly justified, but it seems clear that at room temperature and higher, in the absence of real potential energy terms greater than 100 cal, the molecular shape will be determined predominantly by free rotation.

[6] L. S. Kassel, J. Chem. Phys. **3**, 326–335 (1935).

V. EQUILIBRIUM CONSTANTS FOR REACTIONS OF PARAFFINS, OLEFINS AND HYDROGEN

For the purposes of this section it is necessary to attempt at least a rough treatment of the vibrational contributions to H/T and $-F/T$. The C–C frequencies for the normal hydrocarbons up to butane have been estimated as follows:[6]

Ethane 987 cm^{-1}
Propane 403, 937, 1067 cm^{-1}
Butane, *cis* 221, 492, 879, 1044, 1106 cm^{-1}
trans 312, 385, 974, 987, 1100 cm^{-1}.

The contributions to H/T and $-F/T$ for butane may reasonably be taken as the mean of the not greatly different *cis* and *trans* contributions. Each hydrogen atom introduces one C–H stretching frequency near 3000 cm^{-1}; these frequencies make an almost negligible contribution to the thermodynamic functions except at very high temperatures. The C–H bending frequencies are far more important. In methane[7] they are 1306 (triple) and 1536 (double). There are ten C–H bending frequencies in ethane which have been assigned by Eucken and Parts[8] as follows: 712 (double), 826 (double), 1460 (double), 1465 (double), 1499 (double). A single methyl group has three bending frequencies; thus four of the ten C–H bending frequencies in ethane must depend upon bond angles C–C–H, while six may be determined largely by angles H–C–H. This is a very crude analysis, but it suggests that the former type is to be associated with frequencies near 770 cm^{-1}, the latter with frequencies near 1440 cm^{-1}. Each methylene group in the molecule should then contribute one frequency near 1440 cm^{-1} and three near 770 cm^{-1}; in paraffins with branched chains each CH group contributes two frequencies near 770 cm^{-1}. On this basis the

[7] Childs, Proc. Roy. Soc. **A153**, 555–557 (1936).
[8] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184–194 (1933).

distribution of C−H frequencies in the simpler paraffins is

	770 cm^{-1}	1440 cm^{-1}	3000 cm^{-1}
Methane	0	5	4
Ethane	4	6	6
Propane	7	7	8
Butane	10	8	10
Isobutane	8	9	10

These frequencies have been used to calculate the total vibrational contributions to $-F/T$ and to H/T for methane, ethane, propane and butane given in Table IV. In view of the uncertainty attached to these values, the subsequent calculations will be made so as to defer as long as possible the introduction of vibrational contributions, and to indicate explicitly the net magnitude of those quantities.

The only possible extensive direct comparison with experimental results is for the dehydrogenation reactions; the method of calculation used for these reactions is given in detail for the dehydrogenation of propane. The translation-rotation entropies of Part IV may be combined to give

TABLE IV. *Vibrational $-F/T$ and H/T for hydrocarbons.*

T, °K	Methane	Ethane	Propane	Butane	790 cm^{-1}	572 cm^{-1}	244 cm^{-1}
			$-F/T$				
100	0.000	0.000	0.006	0.057	0.000	0.000	0.055
200	.000	.029	.164	.508	.006	.032	.358
298.1	.005	.219	.691	1.484	.045	.131	.704
300	.005	.223	.703	1.506	.046	.134	.711
355	.025	.426	1.171	2.283	.083	.207	.892
400	.055	.645	1.637	3.023	.121	.274	1.036
500	.160	1.237	2.830	4.862	.218	.429	1.321
600	.323	1.962	4.205	6.917	.326	.586	1.578
673	.479	2.549	5.282	8.498	.409	.697	1.743
700	.548	2.788	5.706	9.117	.440	.739	1.809
800	.820	3.674	7.258	11.359	.554	.882	2.023
900	1.119	4.582	8.818	13.596	.664	1.024	2.203
1000	1.455	5.536	10.431	15.873	.774	1.159	2.376
1100	1.805	6.487	12.016	18.106	.876	1.279	2.531
1200	2.183	7.467	13.630	20.348	.985	1.379	2.680
1300	2.570	8.456	15.244	22.594	1.084	1.507	2.812
1400	2.961	9.414	16.790	24.734	1.173	1.616	2.943
1500	3.359	10.341	18.261	26.769	1.264	1.713	3.069
			H/T				
100	0.000	0.002	0.039	0.222	0.000	0.004	0.200
200	.003	.190	.676	1.446	.040	.137	.707
298.1	.070	.911	2.209	3.778	.173	.374	1.022
300	.070	.929	2.247	3.834	.177	.384	1.027
355	.175	1.516	3.352	5.435	.273	.507	1.146
400	.297	2.052	4.311	6.804	.353	.603	1.224
500	.688	3.355	6.517	9.880	.537	.785	1.356
600	1.179	4.683	8.659	12.803	.670	.930	1.449
673	1.570	5.629	10.137	14.801	.764	1.017	1.501
700	1.730	5.987	10.685	15.532	.796	1.046	1.519
800	2.305	7.238	12.582	18.058	.902	1.147	1.572
900	2.888	8.429	14.354	20.398	.993	1.218	1.616
1000	3.456	9.547	15.996	22.552	1.070	1.283	1.651
1100	4.012	10.599	17.521	24.540	1.137	1.338	1.679
1200	4.545	11.587	18.946	26.392	1.196	1.386	1.704
1300	5.050	12.506	20.259	28.095	1.249	1.426	1.724
1400	5.538	13.375	21.494	29.689	1.291	1.462	1.745
1500	6.002	14.192	22.645	31.172	1.331	1.493	1.757

$$C_3H_8 = C_3H_6 + H_2,$$

$$\Delta(F^\circ - E_0^\circ)/T = -0.876 + 5R \log T + (-F_v/T)_{\text{propane}} - 2.784 - (9R/2) \log T - (-F_{vt}/T)_{\text{propylene}} - (-F/T)_{\text{hydrogen}},$$

where a subscript $_v$ indicates a vibrational contribution excluding torsional vibrations, and a subscript $_{vt}$ indicates vibration including torsion. Values of $(-F/T)_{\text{hydrogen}}$ have been tabulated by Giauque.[9] Then at 673°K,

$$\Delta(F^\circ - E_0^\circ)/T = -27.200 + (-F_{v,\ 673}/T)_{\text{propane}} - (-F_{vt,\ 673}/T)_{\text{propylene}}.$$

The hydrogenation heat determined by Kistiakowsky, Ruhoff, Smith and Vaughan[10] is

$$\Delta H_{355} = 30{,}115$$

$$\text{or} \quad \Delta E_0^\circ = 27{,}998 + (H_{v,\ 355})_{\text{propane}} - (H_{vt,\ 355})_{\text{propylene}}.$$

Hence at 673°K,

$$\Delta F^\circ/T = 14.396 + (-F_{v,\ 673}/T + H_{v,\ 355}/T)_{\text{propane}} - (-F_{vt,\ 673}/T + H_{vt,\ 355}/T)_{\text{propylene}}.$$

The experimental value of Frey and Huppke[11] at this temperature is

$$-R \log K = 12.158.$$

These two theoretically identical expressions will agree if

$$(-F_{vt,\ 673}/T + H_{vt,\ 355}/T)_{\text{propylene}} - (-F_{v,\ 673}/T + H_{v,\ 355}/T)_{\text{propane}} = 2.238.$$

Smith and Vaughan[12] have given 790 cm^{-1} for the torsion frequency in ethylene. If the force constant remains the same, simple reduced mass considerations indicate a value of 572 cm^{-1} for propylene, isobutene and 1-butene, and of 244 cm^{-1} for both 2-butenes. For convenience values of $-F/T$ and of H/T for these frequencies have been included in Table IV. If

[9] Giauque, J. Am. Chem. Soc. **52**, 4816–4831 (1930).
[10] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 876–883 (1935).
[11] Frey and Huppke, Ind. Eng. Chem. **25**, 54–59 (1933).
[12] Smith and Vaughan, J. Chem. Phys. **3**, 341–343 (1935).

this value of 572 cm^{-1} is used for the torsion frequency, the preceding equation becomes

$$(-F_{v,\ 673}/T+H_{v,\ 355}/T)_{\text{propylene}} -(-F_{v,\ 673}/T+H_{v,\ 355}/T)_{\text{propane}}=1.273.$$

Since the olefin, excluding the torsion frequency, has six fewer vibrations than the paraffin, and since there is no reason to expect that any force constants are lowered by the dehydrogenation (it is definitely known that the stretching constant for C=C is greater than that for C−C), one would expect a negative value for the above function. The loss of four CH bending vibrations at 1440 cm^{-1} would make a contribution of −0.49, and consideration of the CC vibrations might easily increase this to −1.0. In order to obtain even a zero value it would be necessary to reduce the experimental equilibrium constant by a factor of 1.90, or to reduce the heat of hydrogenation by 857 cal, or to use a torsion frequency of 250 cm^{-1}.

The results of similar calculations for the other olefins are summarized in Table V. Vibrational functions analogous to those of the preceding two equations are designated δ_{vt} and δ_v, respectively. It will be noted that the various δ_v show a consistency that would be entirely lacking if any constant paraffin-olefin entropy difference had been assumed rather than the actual calculated translation-rotation differences ranging from 3.034 for isobutane to 8.752 for *trans* 2-butene. This consistency was noted in a preliminary report[4] where it was fortuitously somewhat improved by the erroneous estimate there used for 1-butene.

It will be observed that if δ_v is to be made zero by changing the torsion frequencies, the three frequencies estimated at 572 cm^{-1} are changed to an average value of 240 cm^{-1}, and the two estimated at 244 cm^{-1} to an average of 87 cm^{-1}. These are reductions by factors of 0.42 and 0.36. If a mean of 0.39 is applied to the estimate of 790 cm^{-1} for ethylene, the result is 308 cm^{-1}. If the lower dissociation constant for ethane recalculated by Smith and Vaughan from Frey and Huppke's data is used, the result is $\delta_{vt}=0.280$; then 790 cm^{-1} gives $\delta_v=-0.273$ and 308 cm^{-1} gives $\delta_v=-1.699$. This latter value is in fact about what would be calculated from the vibrational frequencies used by Smith and Vaughan. It is utterly impossible. however, to accept such a value for the torsion frequency in ethylene, since it would make a contribution of 0.95 cal./deg. to the heat capacity at 143°K, where Eucken and Parts found a total vibrational heat capacity of only 0.08 cal./deg. Reduction of the δ_v values by manipulation of the assumed torsion frequency is thus out of the question for ethylene, and presumably for the higher olefins as well.

TABLE V. *Comparison of calculated and observed dissociation constants for dehydrogenation reactions.*

Olefin	δ_{vt} (cal./deg.)	δ_v (cal./deg.)	To make $\delta_v=0$: Reduce K by factor of	*or* Reduce ΔH by, (cal.)	*or* Use torsion frequency of, (cm^{-1})
Propylene	2.238	1.273	1.90	857	250
1-Butene	2.471	1.506	2.13	1014	260
Cis 2-Butene	4.343	1.923	2.63	1294	89
Trans 2-Butene	4.427	2.007	2.75	1352	85
Isobutene	2.721	1.756	2.42	1182	210

The ethane figures become more consistent with those for the higher hydrocarbons if the original equilibrium constant of Frey and Huppke is used. This gives $\delta_{vt}=1.456$, and with a torsion frequency of 790 cm^{-1}, $\delta_v=0.903$. To make $\delta_v=0$ it would be necessary to reduce K by a factor of 1.65 or to reduce ΔH by 608 cal. Comparison with experiment may also be made at higher temperatures. Teller and Topley[13] have selected $R \log K=-7.379$ at 863°K as the best value based on all experimental work. This value gives $\delta_{vt}=1.533$, and with a torsion frequency of 790 cm^{-1}, $\delta_v=0.797$.

Thus all these comparisons have given values of δ_v between 0.8 and 2.0, while the value to be expected is in the neighborhood of −1.0. There are five possible interpretations of this discrepancy. The equilibrium constants determined experimentally may be too large by a factor of 3. The hydrogenation heats may be too high by 1500 cal. These seem to be the most reasonable explanations, but it is also conceivable that the low temperature specific heat of ethylene is too low by 1 cal./deg. and hence that the torsion frequencies are much lower than they could otherwise be; or that the other vibrational frequency assignments are quite wrong, so that the only serious error is in the expected value of δ_v; or finally that the paraffin-olefin translation-

[13] Teller and Topley, J. Chem. Soc., July, 876–885 (1935).

rotation entropy differences which have been calculated are 2.5 e.u. too great.

Added in proof, May 29. Dr. F. D. Rossini has kindly given me his preliminary value for the heat of hydrogenation of ethylene, calculated from heats of combustion. The agreement with the direct determination of Kistiakowsky *et al.* is very good. Interpretation of the discrepancy as due to an error in the hydrogenation heats is thus definitely eliminated for ethylene, and rendered unlikely for the higher hydrocarbons.

Although the cause of this disagreement between theoretical and experimental dehydrogenation constants cannot be definitely assigned, it is certainly possible to calculate reliable approximate values for other equilibrium constants. In doing this we shall assume that for any olefin H_v/T and $-F_v/T$ are the same as for the corresponding paraffin as given in Table IV; the torsion contribution from the appropriate frequency, 790, 572 or 244 cm^{-1} must be added to these values. This assumption, which is certainly not literally correct, amounts to assuming a true K value for the dehydrogenations which is smaller than that observed, but larger than that calculated with plausible olefin frequencies.

For the reaction

$$2C_2H_4=CH_2:CHCH_2CH_3$$

we can calculate

$$\Delta H_{298}=-24{,}307 \text{ cal.}$$

by combining Rossini's values for the heats of combustion of hydrogen,[14] ethane[15] and butane[15] with the heat of hydrogenation of ethylene determined by Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan[16] and the heat of hydrogenation of 1-butene.[10] Use of Table IV in the manner stated in the preceding paragraph then gives $\Delta E_0^\circ=-23{,}122$ cal. Then

$$R\log K=8.565-3R\log T+23{,}124/T+(-F_{vt}/T)_{\text{butane}}-2(-F_{vt}/T)_{\text{ethylene}}.$$

In a similar way one finds

$$3C_2H_4=2C_3H_6,$$

$$\Delta H_{298}=-26{,}877 \text{ cal.}, \quad \Delta E_0^\circ=-25{,}354 \text{ cal.},$$

$$R\log K=9.507-3R\log T+25{,}354/T-3(-F_{vt}/T)_{\text{ethylene}}+2(-F_{vt}/T)_{\text{propylene}},$$

$$CH_4+C_2H_4=C_3H_8,$$

$$\Delta H_{298}=-19{,}155 \text{ cal.}, \quad \Delta E_0^\circ=-17{,}692 \text{ cal.},$$

$$R\log K=9.139-3R\log T+17{,}692/T+(-F_v/T)_{\text{propane}}-(-F_v/T)_{\text{methane}}-(-F_{vt}/T)_{\text{ethylene}},$$

$$C_2H_6+C_2H_4=C_4H_{10},$$

$$\Delta H_{298}=-21{,}805 \text{ cal.}, \quad \Delta E_0^\circ=-20{,}559 \text{ cal.},$$

$$R\log K=7.933-3R\log T+20{,}559/T+(-F_v/T)_{\text{butane}}-(-F_v/T)_{\text{ethane}}-(-F_{vt}/T)_{\text{ethylene}},$$

$$CH_4+C_3H_6=C_4H_{10},$$

$$\Delta H_{298}=-16{,}814 \text{ cal.}, \quad \Delta E_0^\circ=-15{,}373 \text{ cal.},$$

$$R\log K=8.095-3R\log T+15{,}373/T+(-F_v/T)_{\text{butane}}-(-F_v/T)_{\text{methane}}-(-F_{vt}/T)_{\text{propylene}},$$

$$H_2+CH_2CHCH_2CH_3=C_4H_{10},$$

$$\Delta H_{298}=-29{,}931 \text{ cal.}, \quad \Delta E_0^\circ=-28{,}044 \text{ cal.},$$

$$R\log K=-3.762+(R/2)\log T+28{,}044/T-(-F/T)_{\text{hydrogen}}-(-F/T)_{572\ cm^{-1}}.$$

TABLE VI. *Values of $\log_{10} K$ for several hydrocarbon reactions.*

T	K_1	K_2	K_3	K_4	K_5	K_6
500	4.405	5.536	1.901	3.099	0.708	6.581
600	2.602	3.574	.457	1.472	−0.570	4.269
700	1.301	2.160	−0.591	.296	−1.501	2.577
800	.308	1.082	−1.395	−0.602	−2.215	1.278
900	−0.472	.235	−2.032	−1.312	−2.784	.243
1000	−1.109	−0.451	−2.553	−1.892	−3.252	−0.605
1100	−1.639	−1.024	−2.988	−2.375	−3.643	−1.313
1200	−2.099	−1.522	−3.363	−2.791	−3.978	−1.913

$K_1=(1-C_4H_8)/(C_2H_4)^2$ $\quad K_4=(C_4H_{10})/(C_2H_6)(C_2H_4)$
$K_2=(C_2H_6)^2/(C_2H_4)^3$ $\quad K_5=(C_4H_{10})/(CH_4)(C_3H_6)$
$K_3=(C_3H_8)/(CH_4)(C_2H_4)$ $\quad K_6=(C_4H_{10})/(H_2)(1-C_4H_8)$

Equilibrium constants calculated from these equations are shown in Table VI.

No entirely convincing estimate of the accuracy of these values is possible, but it would require a highly unfortunate set of cumulative errors to make any of them wrong by a factor greater than 2. Table VI should therefore be useful in the study of cracking reactions, and of the newer polymerization processes for gasoline production.

[14] Rossini, Bur. Standards J. Research **6**, 1–35 (1931).
[15] Rossini, Bur. Standards J. Research **12**, 735–750 (1934).
[16] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65–75 (1935).

Analysis of Rotatory Dispersions of Configurationally Related Halides

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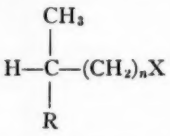
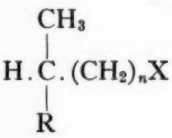
The rotatory dispersion curves of halides of the type



(where X=halogen atom, R=alkyl group) have been analyzed in the visible and the ultraviolet regions. The three halogen atoms function similarly with respect to the character of the rotatory dispersion curve in substances of identical structure. A periodicity is observed in the sign of some of the partial contributions of the halogen atom with the progressive increase in the value of n. The course of the rotatory dispersion of the halides with $n=1$ is anomalous. An attempt was made to apply the results of the observations obtained on substances having $n>0$ to elucidate the sign of rotation of the configurationally related substances having $n=0$.

THE present communication deals with the analysis of rotatory dispersion curves of halides of the general type (I)



where R is an alkyl group, X a halogen atom, and n has the value 0, 1, 2, or 3.

Recent studies have shown that the absorption spectra of organic iodides, bromides and chlorides are analogous.[1, 2] With decreasing wave-lengths there is found first, a broad region of continuous absorption with a maximum located at λ2600 for the iodides, λ1900 for the bromides, and λ1720 for the chlorides. For smaller wave-lengths, the absorption may be resolved into lines which fit two series of Rydberg. They converge towards two limits corresponding to the respective ionization potentials.

Although experimental proof is lacking so far, it might be assumed that all the rotatory contributions of the terms belonging to the same Rydberg series are of the same sign. In this case, their sum should be expressed with a fair degree of accuracy for the near ultraviolet and the visible regions, by a one-term Drude formula with a dispersion constant located between the first term and the limit of the series. Three dispersion terms might then be required to take care of the rotatory contribution of the halogen atom in the halides, one corresponding to the continuum, and the other two to the two Rydberg series.

In Table I are given the rotations for the sodium D line of the members of several homologous series of bromides of the general formula I having $n>0$. It can be seen from this table that with the change of the value of n from 1 to 2 there is observed an increase in the rotation (in the case given in Table I a shift of the rotation to the right). On further increase of the value of n to 3 the value of the molecular rotation drops (shift of the rotation to the left). Thus a periodicity is observed in the direction of the shift of rotation on progressive increase in the value of n.

It was desired (by means of analysis of the rotatory dispersion curves of these substances) to answer the question as to the part the halogen atom plays in the rotatory events associated with the progressive increase in the value of n. On the assumption that the corresponding absorption bands in the iodides, bromides, and chlorides function similarly with respect to their rotatory powers, it was deemed advantageous to extend the analysis of the rotatory dispersions to the iodides and chlorides. The iodides offer an advantage by virtue of the relative proximity of their first continuum and second absorption region, and the chlorides by virtue of their greater transparency.

Table II contains the composite results of the direction and of the relative magnitude of the

* The part of Mr. Marker consisted in the preparation of the substances marked by an asterisk.

[1] W. C. Price, Phys. Rev. **47**, 419 (1935).

[2] W. C. Price, Phys. Rev. **47**, 510 (1935).

TABLE I. *Configurationally related bromides* $[M]_D^{25}$ Max. (homogeneous).

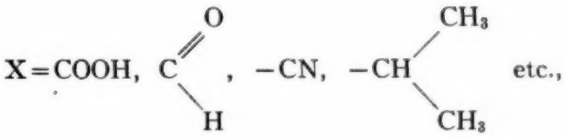
CH_3 H.C.CH_2Br C_2H_5	CH_3 H.C.$(CH_2)_2Br$ C_2H_5	CH_3 H.C.$(CH_2)_3Br$ C_2H_5	CH_3 H.C.$(CH_2)_4Br$ C_2H_5	CH_3 H.C.$(CH_2)_5Br$ C_2H_5
+7.9	+38.8	+21.9	+14.9	+14.0
CH_3 H.C.CH_2Br C_3H_7	CH_3 H.C.$(CH_2)_2Br$ C_3H_7	CH_3 H.C.$(CH_2)_3Br$ C_3H_7	CH_3 H.C.$(CH_2)_4Br$ C_3H_7	
low dextro	+21.0	+14.5	+7.8	
CH_3 H.C.CH_2Br C_4H_9	CH_3 H.C.$(CH_2)_2Br$ C_4H_9	CH_3 H.C.$(CH_2)_3Br$ C_4H_9	CH_3 H.C.$(CH_2)_4Br$ C_4H_9	
low dextro	+16.8	+8.3	+5.3	
CH_3 H.C.CH_2Br C_5H_{11}	CH_3 H.C.$(CH_2)_2Br$ C_5H_{11}	CH_3 H.C.$(CH_2)_3Br$ C_5H_{11}	CH_3 H.C.$(CH_2)_4Br$ C_5H_{11}	
low dextro	+14.7	+6.2	+4.0	

rotation of each absorption region of the halogen atom.

With the progressive increase in the value of n it can be seen from this table that in the members having $n \geq 1$, the direction of the partial rotation of the second and third absorption regions displays a periodic change which is associated in the visible region with a periodic change in the direction of the shift of rotation. From the dispersion formulae given in the last paragraph it may be seen that the partial rotations of the halogen atoms constitute the major contributions to the rotation of the halides in the visible region.

The members having $n=0$ cannot be correlated by the methods of classical organic chemistry to those having $n \geq 1$ and therefore the direction of their partial rotation is not given in Table II.

It was desired to attempt this correlation on the basis of observations on substances of the same general formula (I) but with



in which all members can be correlated by methods of classical organic chemistry.

The rotatory events in the latter substances are illustrated best in the case of the aldehydes,[3] in which there is observed: first, a change of sign in the partial rotation of the functional group on passing from $n=0$ to $n=1$, and second, a periodicity in the direction of the shift of this partial rotation with progressive increase of the value of n (from 0 to 3).

It is now proposed to assign alternately the signs plus and minus to the first three absorption regions of the halogen atom of the members having $n=0$ and then to compare the course of events in the series thus formed with respect to n with that in the series represented by the aldehydes.

By assigning levorotation to the members having $n=0$, a series emerges which resembles that of the aldehydes in that the change of n

TABLE II. *Directions and relative values of the partial contributions of the halogen atom in halides of the general formula (I).*

n	0	1	2	3
First band	moderate	0	(≷0)	0
Second region	strong	−	++	0
Third region	weak	++	−	++
Fourth (in the main in rest of the molecule)	of opposite sign	?	?	−

[3] P. A. Levene and A. Rothen, J. Chem. Phys. **4**, 48 (1936).

from 0 to 1 brings about a change in the direction of the partial rotation of X; it differs from the aldehyde series in that the periodicity in the direction of the shift of rotation with the progressive increase in the value of n begins not with the member having $n=0$, but with that having $n=1$.

By assigning dextrorotation to the members having $n=0$, a series is obtained which resembles that of the aldehydes in that there is a periodicity in the direction of the shift of rotation beginning with the member having $n=0$; it differs from the aldehyde series in that the change of $n=0$ to $n=1$ is not associated with a change in the direction of rotation of the two members.

Hence, whatever sign is attributed to the members having $n=0$, no complete analogy exists between the series where X is a halogen atom with those in which X equals one of the above-mentioned groups.

Thus the problem of the correlation of the configurations of the halides having $n=0$ to those having $n=1$ must await for its solution the development of a physical theory of optical rotation more satisfactory than those now in existence and capable of explaining on a rational basis the events in the series in which the members having $n=0$ have been correlated to those having $n>0$ by methods of classical organic chemistry. The theoretical models suggested, and the mathematical formulae developed to date fail to do this.

Recently Kuhn[4] suggested a model on the basis of which he formulated the absolute configuration of secondary carbinols. His model is inadequate to explain the difference in the sign of rotation of two configurationally related carbinols, 2-methylpentanol-1 and 2-ethylpentanol-1. Hence it is at best not sufficiently comprehensive. In fact, his formulation of the absolute configuration of secondary carbinols is doubtful. However, if a satisfactory model could be constructed based on Kuhn's theory that the direction of polarizibility and of the electric moment of a group may determine the sign of its rotatory contribution, then in such a model a change of direction of 90° of the vibration should produce a reversal of sign of rotation. The periodicity observed in some of the partial rotations of a functional group could very well be produced by this phenomenon, since the angle made by the bond joining the functional group to the rest of the molecule and the line joining two of the three other groups attached to the asymmetric carbon atom, varies periodically with n if one considers a restricted free rotation.

[4] W. Kuhn, Zeits. f. physik. Chemie **B31**, 23 (1935).

Absorption Spectra

The absorption curves of the continuum of the iodides may be seen in Fig. 1. They remain practically unchanged in magnitude and position with the variation of n. There is a difference of about 60A in the position of the maximum in the secondary iodides as compared with the primary. The uniformity met within the absorption curves contrasts sharply with the state of affairs found in the rotatory dispersions of the same compounds.

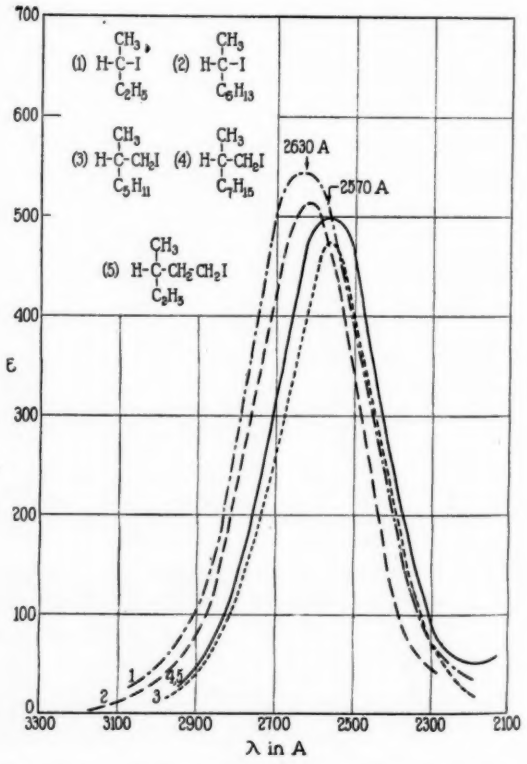


FIG. 1. Absorption spectra of iodides (ϵ = molecular extinction coefficient).

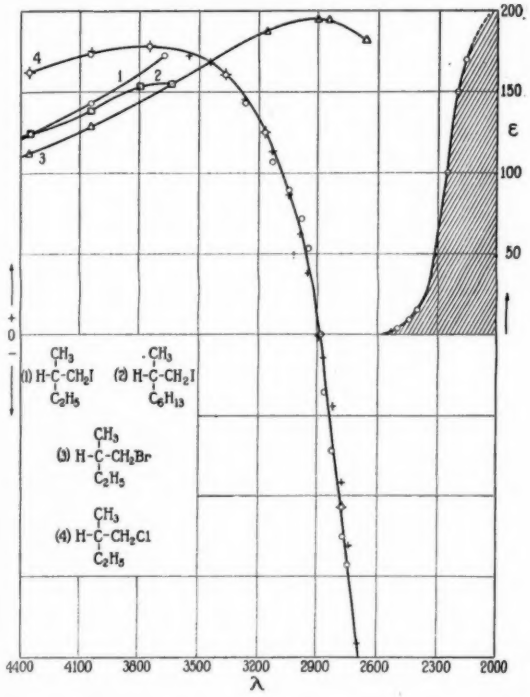


FIG. 2. Rotatory dispersion curves of primary halides. The ordinate represents the rotations in arbitrary units. The absorption curve of the bromide may be seen to the right (shaded surface).

ROTATORY DISPERSION CURVES

Experimental data concerning the rotatory dispersions are summarized in Tables IV to VI and in Fig. 2. In order to save space, only the observed rotations have been given for the iodides. A two-term formula has been calculated for each compound, which reproduces the observed dispersion curve within experimental errors (0.05 percent in the visible, and about 1 percent in the ultraviolet region). The numerators of the terms have been so adjusted that the formulae express the maximum rotations. The maximum values are, of course, very approximate, but their order of magnitude is correct.

TABLE III. *Configurationally related halides.*

COMPOUNDS	$[M]_D^{25}$ max	n_D^{25}	d_4^{25} (in vacuum)
Levo 2-iodobutane*	−58.8	1.4975	1.589
Levo 2-iodooctane	−97.4	1.4863	1.3158
Dextro 1-iodo-2-methylbutane*	11.2	1.4950	1.5138
Dextro 1-iodo-2-methylheptane	5.0	1.4875	1.3331
Dextro 1-iodo-2-methylnonane	5.0	1.4850	1.2536
Dextro 1-iodo-3-methylpentane	47.0	1.4884	1.4187
Dextro 1-iodo-4-methylhexane	26.7	1.4893	1.3480
Levo 2-bromobutane*	−30.0	—	1.2536
Levo 2-bromooctane	−62.5	1.4484	1.0983
Dextro 1-bromo-2-methylbutane	7.9	1.4426	1.2144
Dextro 1-bromo-3-methylpentane*	38.8	1.4468	—
Levo 2-chlorooctane	−39.5	1.4247	0.8613
Dextro 1-chloro-2-methylbutane	1.7	1.4101	0.8810
Dextro 1-chloro-3-methylheptane	7.9	1.4289	—
Dextro 1-chloro-4-methylhexane	21.0	1.4228	0.8702
Dextro 1-chloro-5-methylnonane	2.3	1.4364	0.8690

In Table III the maximum $[M]_D$ values have been tabulated for all the compounds studied. It may be seen from Table IV and related equations, that the secondary iodides have their first two absorption regions active.[5] The contribution of the first continuum is important, and the fact that both contributions are of the same

[5] In this connection we wish to refer to a recent article of Kuhn, Zeits. f. physik. Chemie **B29**, 256 (1935), criticizing our interpretation of the dispersion of the iodides, already published by us in a short note, P. A. Levene and A. Rothen, Am. Chem. Soc. **55**, 429 (1935). His contention that the rotatory contribution of the continuum of the iodides is negligible seems in accord with his published rotatory dispersion curve. A comparison of our measurements with his curve, however, shows a great discrepancy between his experimental values and our own (it is unfortunate that Kuhn's failure to give figures besides his curves makes a precise comparison difficult). Taking at random a few values brought to coincide at λ5000, ($\alpha = 100$) we found, $\alpha_{4000} = 230$ (Kuhn), $\alpha_{4000} = 185.4$ (Levene and Rothen); $\alpha_{3000} = 1000$ (Kuhn), $\alpha_{3000} = 613$ (Levene and Rothen); $\alpha_{2300} = 1400$ (Kuhn), $\alpha_{2300} = 600$ (Levene and Rothen). We are at a loss to explain this difference. We duplicated our measurements (see below) on different samples of 2-iodooctane and determined the dispersion of the lower homolog 2-iodobutane, which has been found analogous. The difference between the dispersion in heptane and in homogeneous state has been found very small. Our measurements were made with two different polariscopes, one for the visible, and one for the ultraviolet regions. The data so obtained were consistent. The measurement made at λ4046.6, the smallest wave-length used in the visible region, already indicates that the curvature of the dispersion curve is that required by two terms of the same sign, the first one corresponding to the continuum. Kuhn criticizes our interpretation, based on extrapolation. We agree that, as a rule, extrapolation methods are treacherous, but when absorption makes it impossible to obtain good experimental values, they have to be resorted to. The results so obtained are correct, provided: First, that extrapolation is not extended too far; second, that the experimental values used for the extrapolation are of a high degree of accuracy. Both conditions were fulfilled in our work. In the case of the secondary iodides, for instance, we predicted that the first continuum was active from extrapolated values; actual measurements made later on on the short wave-length side of the band confirmed our prediction. Furthermore, Kuhn compares his results obtained on secondary iodides with our results on primary iodides ($n = 1$), taking for granted that the dispersion of the latter is comparable to that of the former. From that comparison Kuhn concludes that our results ($n = 1$) are erroneous. Our present article shows that such comparisons are not legitimate. What is true concerning the partial rotatory contributions of the different bands of the iodine atom, in a compound in which n has a certain value, cannot be applied to those in which n has a different value. The distance of the chromophoric group from the asymmetric carbon atom is of the utmost importance, a factor as essential, in a way, as the order in which the three other groups attached to the asymmetric carbon atom are arranged.

TABLE IV. *Experimental rotatory values (homogeneous state) of configurationally related iodides.*

	Levo 2-Iodobutane	Levo 2-Iodooctane	Dextro 1-Iodo-2-Methylbutane	Dextro 1-Iodo-2-Methylheptane	Dextro 1-Iodo-2-Methylnonane	Dextro 1-Iodo-3-Methylpentane	Dextro 1-Iodo-4-Methylhexane
$\alpha^{25}_{5875.6}$		48.265 (10 cm)	5.439 (10 cm)	5.518 (40 cm)		12.977 (10 cm)	4.987 (10 cm)
$\alpha^{25}_{5780.1}$	6.672 (20 cm)	50.186	5.626	5.696	1.242 (10 cm)	13.468	5.172
$\alpha^{25}_{5460.7}$	7.670	57.613	6.314	6.325	1.374	15.390	5.873
$\alpha^{25}_{4358.3}$	13.988	104.16	9.91_5	9.225	2.01	27.01	9.94
$\alpha^{25}_{4046.6}$	17.51	129.63	11.45_8	10.16	2.23	33.03	11.96
α^{25}_{3780}	5.40 (5 cm)		6.90 (5 cm) for λ3680	1.40 (5 cm) from λ3800 to λ3640	1.25 (5 cm) from λ3850 to λ3600		
α_{3710}		86.15 (5 cm)				22.8 λ3628 (5 cm)	1.8 λ3500 (1 cm)
α_{3685}		88.15				23.8 λ3580	1.9 λ3450
α_{3368}		19.82 (1 cm)				2.72 λ3445	
α_{2300}		0.07 (0.1 cm) conc. 0.155M in heptane					

sign explains the high rotation observed in the visible region. On the other hand, the first continuum in iodides for which $n=1$ seems but slightly active, and the two rotatory contributions due to the second and third absorption regions are of opposite sign; hence a low value for the maximum rotation in the visible region. The second rotatory component is even greater than the first in the visible and near ultraviolet regions, with the result that the dispersion curve becomes anomalous. In the corresponding chlorides it is possible to observe that, with decreasing wave-lengths, the rotation goes through a maximum, reaches zero and increases in the opposite sense. The maximum could be reached in the bromides, but not in the iodides (see Fig. 2). These facts are easily understood if one considers that the wave-length interval between the inactive continuum and the first lines of the Rydberg series is much greater in the iodides than in the other halides. Similar considerations explain the failure to detect the contribution furnished by the third region (see Table II) in secondary and primary iodides having $n=2$. In this case, the contributions of the continuum and second absorption region predominate and mask the other contribution completely.

The rotatory dispersion of the secondary halides needs special consideration. From the dispersion equations it may be seen that it is only in the case of the iodides that the dispersion

TABLE V. *Rotatory dispersion of configurationally related bromides.*

Levo 2-Bromobutane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=5$ cm and 1 cm from λ2827 to λ2745.

λ	α^{25}	$[M]^{25}_{max.}$
5780.1	42.782	31.333
5460.7	48.757	35.709
4358.3	84.01	61.53
4046.6	101.68	74.47
3797	30.1	88.2
3630	34.1	99.9
3490	38.1	111.6
3382	42.1	123.3
3259	47.1	138.0
3139	53.1	155.5
3040	59.1	173.1
2827	15.1	221
2790	16.1	236
2765	16.6	243
2745	17.1	250

Levo 2-Bromooctane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=10$ cm, 5 cm from λ2932 to λ2870, 1 cm from λ2842 to λ2823, 0.1 cm for λ2710 and λ2633.

λ	α^{25}	$[M]^{25}_{max.}$
5875.6	51.622	62.927
5780.1	53.525	65.247
5460.7	60.960	74.310
4358.3	104.47	127.35
4046.6	126.19	153.82
3378	103.8	253.1
3274	113.8	277.4
3190	123.8	301.8
3113	133.8	326.2
3075	138.8	338.4
3044	143.8	350.6
3010	148.8	362.8
2982	153.8	375.0
2932	81.8	398.8
2891	85.8	418.4
2870	87.8	428.1
2842	18.1	441
2823	18.6	453
2710	2.25	548
2633	2.55	622

Dextro 1-Bromo-2-Methylbutane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=5$ cm and 0.5 cm for λ2660.

λ	α^{25}	$[M]^{25}_{max.}$
5875.6	5.024	7.938
5780.1	5.192	8.203
5460.7	5.806	9.173
4358.3	8.965	14.165
4046.6	10.30	16.27
3160	3.75	23.7
2900	3.90	24.6
2845	3.90	24.6
2660	0.37	23

Dextro 1-Bromo-3-Methylpentane in Heptane. Visible region: conc. 0.6037M. $l=40$ cm. U.V. region: conc. 0.9146M $l=10$ cm.

λ	α^{25}	$[M]^{25}_{max.}$
6678.1	3.40	30.0
5875.6	4.446	39.24
5780.1	4.578	40.41
5460.7	5.205	45.94
4358.3	8.765	77.36
3445	6.10	142
3250	7.10	165
3170	7.60	177
3000	9.10	212
2845	10.60	247
2745	11.90	282

TABLE VI. *Rotatory dispersion of configurationally related chlorides.*

LEVO 2-CHLOROOCTANE WITHOUT SOLVENT. Visible region: $l=20$ cm, U.V. region: $l=10$ cm, 5 cm for λ2460 to λ2396, 1 cm for λ2348, 0.1 cm for λ2240.

λ	α^{25}	$[M]^{25}_{max.}$
5875.6	42.402	39.758
5780.1	43.965	41.224
5460.7	49.883	46.773
4358.3	83.775	78.552
4046.6	100.17	93.92
3868	56.1	105.2
3736	61.1	114.6
3622	66.1	124.0
3521	71.1	133.3
3352	81.1	153.4
3218	91.1	170.8
3100	101.1	189.6
3000	111.4	208.9
2915	121.1	227.1
2838	131.1	245.8
2460	105.1	394.2
2412	113.1	424.2
2396	116.1	435.4
2348	25.1	471
2240	3.1	580

DEXTRO 1-CHLORO-2-METHYLBUTANE WITHOUT SOLVENT. Visible region: $l=10$ cm, U.V. region: $l=5$ cm and 1 cm for λ2495 to λ2360.

λ	α^{25}	$[M]^{25}_{max.}$
5875.6	0.596	1.751
5780.1	0.612	1.798
5460.7	0.666	1.959
4358.3	0.91	2.67
4046.6	0.97	2.84
3750	0.50	2.94
3550	0.50	2.94
3370	0.45	2.64
3270	0.40	2.36
3170	0.35	2.06
3050	0.25	1.46
2990	0.20	1.17
2980	0.15	0.87
2885	0.00	0.00
2870	−0.10	−0.58
2830	−0.20	−1.18
2785	−0.30	−1.76
2750	−0.40	−2.35
2495	−0.40	−11.8
2440	−0.50	−14.7
2400	−0.60	−17.6
2360	−0.70	−20.5

DEXTRO 1-CHLORO-3-METHYLHEPTANE WITHOUT SOLVENT. Visible region: $l=20$ cm, U.V. region: $l=5$ cm and 1 cm for λ2750.

λ	α^{25}	$[M]^{25}_{max.}$
5892.6	5.013	7.892
5780.1	5.242	8.252
5460.7	5.958	9.380
4358.3	10.135	15.955
4046.6	12.16	19.14
3630	4.1	25.8
3340	5.1	32.1
3050	6.6	41.6
2860	8.1	51.0
2750	1.85	58.2

DEXTRO 1-CHLORO-4-METHYLHEXANE WITHOUT SOLVENT. Visible region: 20 cm, U.V. region: 5 cm and 1 cm for λ2596 to λ2415.

λ	α^{25}	$[M]^{25}_{max.}$
5875.6	7.856	21.140
5780.1	8.142	21.910
5460.7	9.219	24.808
4358.3	15.375	41.374
4040.6	18.27	49.16
3180	8.38	90.2
3115	8.88	95.6
2990	9.88	106.3
2900	10.88	117.1
2845	11.38	122.5
2803	11.88	127.9
2765	12.38	133.2
2690	13.38	144.0
2595	3.00	161
2460	3.50	188
2415	3.65	196

DEXTRO 1-CHLORO-5-METHYLNONANE WITHOUT SOLVENT. Visible region: $l=20$ cm, U.V. region: $l=5$ cm.

λ	α^{25}	$[M]^{25}_{max.}$
5875.6	1.528	2.303
5780.1	1.578	2.378
5460.7	1.800$_5$	2.714
4358.3	3.075	4.635
4046.6	3.68	5.55
3540	1.35	8.14
3300	1.60	9.65
3135	1.85	11.1

curve may be expressed by two terms of the same sign, corresponding to the first two absorption regions. If one term is tried to reproduce the experimental curve, the dispersion constant falls between these two absorption regions and with the progressive decrease in wave-lengths, the rotations increase more rapidly than is to be expected from a single-term Drude formula. At first sight, the corresponding bromides and chlorides seem to behave differently. If the $1/[M]$ values are plotted against λ^2, the slight curvature observed is opposite to that found in the iodides. There is no doubt that the two main rotatory terms are of opposite sign. The transparency of 2-chlorooctane permitted rotatory measurements very far into the ultraviolet region. A careful analysis showed that when a two-term formula was tried, the dispersion constant of the first and more important term was located between the first two absorption regions. This fact indicates that this term represents the contributions of the first two absorption regions and that they are of the same sign as in the case of the iodides. The dispersion constant of the second term was negative, thus showing definitely that the term was anomalous, i.e., the third contribution was smaller than the the fourth, and of opposite sign. A three-term formula has been calculated, the first term taking care of the rotatory contributions of the first and second absorption regions, the second and third terms representing the third and fourth rotatory contributions, respectively. It is probably true that for the most part the fourth contribution originates in the rest of the molecule (alkyl groups) and cannot be detected in the iodides owing to the great proximity of the first continuum. The dispersion constants of the second and third dispersion terms (corresponding to the third and fourth absorption regions) cannot be considered as significant since they can be changed slightly and still express the experimental values with a reasonable degree of accuracy.

The same state of affairs is found in the secondary bromides. The analysis of their rotatory dispersion curves proved more difficult, on account of the following facts:

1. The departure of the function $1/[M]=f(\lambda^2)$ from a linear relation was very small, only one percent over the whole wave-length interval studied.

2. The absorption of the compound prevented measurements over a region of the spectrum as broad as in the case of the chlorides. A three-term

formula has been calculated for 2-bromooctane (see Table V) in spite of the fact that one term is nearly satisfactory, the dispersion constant of the latter being, of course, greater than that of the first term of the three-term formula. The three-term formula corresponds to that calculated for 2-chlorooctane, the first term, as we have seen, representing the sum of the first two contributions which are of the same sign. It should be expected that as the region of the first continuum is approached, the value of its rotatory contribution should become greater than the calculated one included in the first term. In fact, it is seen that when the $1/[M]$ values are plotted against λ^2, a slight concave curvature is observed in the visible and near ultraviolet regions because the influence of the fourth contribution is greater than that of the first. For low values of λ however, the curvature becomes convex, the effect of the first contribution outbalancing that of the fourth contribution.

In the secondary bromides, the only case where it could be tested—the rule previously enunciated has been verified, namely, that *in a homologous series with respect to R, if the dispersion can be expressed by two terms of opposite sign, then, for any two members, the one with the greater dispersion has the smaller maximum rotation.*

It may be added that on account of the mentioned periodicity observed in the partial rotations of the halogen atom in a series homologous with respect to *n*, a corresponding periodic effect is observed in the dispersion ratios of the molecule as a whole. The following ratios $R=\alpha_{4046.6}/\alpha_{5780.1}$ for the series of chlorides brings out clearly the phenomenon:

2-chlorooctane $R=2.278$, 1-chloro-2-methylbutane $R=1.58$, 1-chloro-3-methylheptane $R=2.320$, 1-chloro-4-methylhexane $R=2.244$.
1-chloro-5-methylnonane $R=2.332$.

EQUATIONS REPRESENTING THE MAXIMUM MOLECULAR ROTATIONS OF THE IODIDES, BROMIDES AND CHLORIDES, VALID IN THE VISIBLE AND THE NEAR ULTRAVIOLET SPECTRUM

Levo 2-iodobutane:

$$[M]^{25}_{max.}=-\frac{9.8023}{\lambda^2-0.0685}-\frac{7.2490}{\lambda^2-0.040}$$

(in homogeneous state).

The value $[M]_D^{25}=-58.8$ was taken as maximum.[6] The dispersion of this compound was also taken in heptane. The molecular rotations were 1.49 percent higher than in homogeneous state. The dispersion was practically the same. (If a one-term Drude formula is used to express the dispersion from two given λ, a difference of only 8A is found between the two dispersions constants of the terms corresponding to the measurements in the homogeneous state and in heptane.)

Levo 2-iodooctane:

$$[M]^{25}_{max.}=-\frac{13.312}{\lambda^2-0.069}-\frac{15.162}{\lambda^2-0.040}$$

(in homogeneous state),

$$[M]^{25}_{max.}=-\frac{12.226}{\lambda^2-0.069}-\frac{18.175}{\lambda^2-0.040}$$ (in heptane).

The dispersion is slightly more susceptible to the effect of the solvent than in the case of the 2-iodobutane. The rotation is about 6.0 percent greater in heptane than in homogeneous state for λ5780.1. The order of magnitude of the rotation on the short wave-length side of the first band is for λ2300, $[M]_{2300}=500°$. The value calculated from the above equation which should hold only approximately for that region is $[M]_{2300}=630°$.

Two samples were prepared, both gave the same dispersion in spite of the fact that one of them had too low a density and index of refraction (some iodine split off, inactive impurity).

Dextro 1-iodo-2-methylbutane:

$$[M]^{25}_{max.}=-\frac{4.7539}{\lambda^2-0.043}+\frac{8.5535}{\lambda^2-0.028}.$$

Dextro 1-iodo-2-methylheptane:

$$[M]^{25}_{max.}=-\frac{4.4216}{\lambda^2-0.046}+\frac{6.2033}{\lambda^2-0.032}.$$

Dextro 1-iodo-2-methylnonane:

$$[M]^{25}_{max.}=-\frac{5.707}{\lambda^2-0.040}+\frac{7.527}{\lambda^2-0.028}.$$

Dextro 1-iodo-3-methylpentane:

$$[M]^{25}_{max.}=\frac{14.133}{\lambda^2-0.0466}.$$

Dextro 1-iodo-4-methylhexane:

$$[M]^{25}_{max.}=\frac{8.377}{\lambda^2-0.0336}.$$

Levo 2-bromobutane:

$$[M]^{25}_{max.}=-\frac{12.6140}{\lambda^2-0.032}-\frac{3.482}{\lambda^2}.$$

Levo 2-bromooctane:

$$[M]^{25}_{max.}=-\frac{22.159}{\lambda^2-0.034}-\frac{2.540}{\lambda^2-0.025}+\frac{5.434}{\lambda^2-0.010}.$$

Dextro-1-bromo-2-methylbutane:

$$[M]^{25}_{max.}=-\frac{9.4151}{\lambda^2-0.032}+\frac{12.169}{\lambda^2-0.025}.$$

[6] R. H. Pickard and R. J. Kenyon, J. Chem. Soc. 99, 45 (1911).

Dextro-1-bromo-3-methylpentane:

$$[M]^{25}_{max.} = \frac{12.243}{\lambda^2 - 0.0317}.$$

Levo 2-chlorooctane:

$$[M]^{25}_{max.} = -\frac{15.966}{\lambda^2 - 0.024} - \frac{7.329}{\lambda^2 - 0.020} + \frac{10.820}{\lambda^2 - 0.012}.$$

Dextro 1-chloro-2-methylbutane:

$$[M]^{25}_{max.} = -\frac{3.667}{\lambda^2 - 0.030} + \frac{4.352}{\lambda^2 - 0.020}.$$

Dextro 1-chloro-3-methylheptane:

$$[M]^{25}_{max.} = \frac{4.6373}{\lambda^2 - 0.025} - \frac{2.1879}{\lambda^2 - 0.015}.$$

Dextro 1-chloro-4-methylhexane:

$$[M]^{25}_{max.} = \frac{13.915}{\lambda^2 - 0.015} - \frac{7.249}{\lambda^2}.$$

Dextro 1-chloro-5-methylnonane:

$$[M]^{25}_{max.} = \frac{1.763}{\lambda^2 - 0.025} - \frac{1.059}{\lambda^2 - 0.015}.$$

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Remarks Concerning the Formation and Crystallization of Vitreous Media

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The various characteristics of the liquid-glass transition are examined in an attempt to establish the hypothesis that liquid or vitreous properties depend upon the relation between the thermal relaxation time and the time of measurement, and not upon any discontinuous allotropic change at a fixed temperature. In the course of this survey it is found that the relaxation time involved in the liquid-glass transition for the heat capacity of glucose must be far less than that for the molecules, and is therefore probably that characterizing rotations of groups within the molecules, or certain modes of vibration of atoms or groups. No need is found from any of the measurements examined for the postulation of a "vitreous state of aggregation," since all the properties of glasses appear to be those of undercooled liquids of high viscosity. Since the viscosity of laboratory glass is too high to permit its devitrification within a reasonable time, a mechanism involving surface solution is suggested by means of which observed phenomena may be explained.

INTRODUCTION

IN recent years much interest has been aroused by the vitrification of viscous liquids. From a theoretical standpoint the matter gives a promising attack on some aspects of the liquid state, and it has yielded indispensable information concerning annealing schedules and the like. It is not intended here to give an historical résumé of the subject, since it is not felt that the thesis about to be expounded is either sufficiently complex or fundamental to justify an elaborate introduction. Such references as are made to the literature of the subject will, therefore, be chosen merely for illustrative purposes, without regard to completeness or sequence.

Numerous authors have reported abrupt changes in the temperature derivatives of the heat content, specific volume, and like properties over short temperature ranges for a wide variety of substances in the amorphous state, while the properties themselves appear to undergo no change. The temperature at which the derivatives change is known variously as the glass temperature, the temperature of maximum association, the vitrification point, etc., and is generally designated by T_g. The interpretation of these changes is, however, diverse. One school of thought considers that they indicate an allotropic change to a new state of aggregation. Le Chatelier[1] suggested this some years ago on the basis of viscosity data. Recently Mondain-Monval,[2] who is perhaps the most radical of the group in his views, wrote (p. 22), "We are resolutely partisan to the hypothesis of an allotropic transformation characteristic of the amorphous state" and, concerning T_g (p. 69) "there exists, then, . . . a unique temperature below which the stable crystalline variety cannot appear . . . by crystallization of the body in the vitreous state." Similarly Kobeko and his associates[3–7] consider

[1] H. le Chatelier, Ann. de physique **3**, 5 (1925).
[2] P. Mondain-Monval, Ann. de Chimie **3**, 1 (1935).
[3] P. P. Kobeko, Physik. Zeits. Sowjetunion **4**, 83 (1933).
[4] Kobeko and I. J. Nelidow, ibid. **4**, 516 (1933).
[5] Kobeko and E. Kuwschinsky, ibid. **4**, 680 (1933).
[6] Kobeko and I. J. Nelidow, ibid. **4**, 695 (1933).
[7] Kobeko and I. J. Nelidow, ibid. **4**, 703 (1933).

T_g the point where the association of the glass has reached its maximum possible value. Sharply opposed to these opinions is the view of Littleton,[8] who writes "there are no critical temperatures in the properties of glasses. There is a change . . . which occurs at all temperatures until stabilization has taken place." In support of this view may be cited especially the viscosity measurements of Lillie,[9] which will receive further attention below. In sympathy with this Morey[10] writes "it should be emphasized that discontinuities, found from measurements with continually changing temperature on properties which not only change with temperature, but also require considerable time to reach an equilibrium value, cannot be admitted as evidence of a real change in the condition of the glass." In direct contradiction to the hypothesis of Mondain-Monval, Morey states that silicate glasses may be crystallized without difficulty below the "transition temperature" by long heating. Parks, Thomas and Light[11] comment "a thorough test of these opposing views . . . is probably impossible in the case of heat capacity data because calorimetric procedures, at least at the present day, do not permit accurate measurements over such (long) periods of time." It is hoped that this communication may provide a solution for this very real difficulty.

One further highly important difference of opinion should be mentioned, in this case concerning facts and not interpretation. In general those writers who believe T_g to be a unique characteristic temperature corresponding to a fusion or transition point naturally consider that all the properties of the glass change at this temperature, whereas those who attribute to it a much less profound significance prefer to stress the divergent temperatures at which the liquid-glass transition occurs for different properties and methods of measurement. Choosing, again, an extreme view we may cite Rencker:[12] "the differences between the points of transformation defined by various physical properties are of the order of experimental error." Koerner and Salmang[13] on the other hand report a variation of 50°C in the transformation point as defined by the thermal expansion coefficient alone, caused by varying the heat treatment of the glass. Parks and his associates, who clearly endeavor to remain impartial, report for glucose glass that the heat capacity transition occurs at 7°C, the expansion coefficient at 24°C and the dielectric constant transition at 1000 kc at 77°C. Similar disparities appear with the other substances which they have investigated.

It is proposed, in the following discussion, to adopt the standpoint of Littleton and to examine the characteristics of the liquid-glass and glass-crystal transitions with the aid of the conception of the thermal relaxation time. Thus a glass will be considered as an undercooled liquid which differs in no respect from any other undercooled liquid in behavior or properties. It should be understood, however, that the elimination of a "vitreous state of aggregation" from the discussion is not intended to exclude the formation of more or less oriented aggregates of molecules which is usually referred to as "association." Such aggregates have been shown to exist in undercooled benzophenone by light-scattering measurements even when the liquid has a very low viscosity,[14] and it is believed that increasing "association" with decreasing temperature is a necessary condition for great undercooling. It is here intended to demonstrate that, because of the increase of thermal relaxation time, any undercooled liquid must pass into the vitreous state with decreasing temperature independent of its "degree of association," that this transition must appear to be abrupt for any given property, and that it must occur at different temperatures for different properties.

The Thermal Relaxation Time

The formulation of an expression for the thermal relaxation time follows from the discussion of the Brownian motion given by Einstein.[15] For a sphere of radius r in a con-

[8] J. T. Littleton, Ind. Eng. Chem. **25**, 748 (1933).
[9] H. R. Lillie, J. Am. Ceram. Soc. **16**, 619 (1933).
[10] G. W. Morey, J. Am. Ceram. Soc. **17**, 315 (1934).
[11] G. S. Parks, S. B. Thomas and D. W. Light, J. Chem. Phys. **4**, 64 (1936).
[12] E. Rencker, Ann. de Chimie **3**, 533 (1935).
[13] Koerner and Salmang, Zeits. f. anorg. allgem. Chemie **199**, 235 (1931).
[14] W. T. Richards and P. M. Harris, J. Am. Chem. Soc. **54**, 3799 (1932).
[15] A. Einstein, Ann. d. Physik **17**, 549 (1905); **19**, 371 (1906).

tinuous medium of viscosity η the mean of the squared angle of rotation $\overline{\omega^2}$ in a time t is

$$\overline{\omega^2}/t = kT/4\pi\eta r^3$$

where kT is $\frac{2}{3}$ of the translational energy. This conception was subjected to a daring simplification by Debye,[16] who considered that it would apply equally to a spherical molecule surrounded by a medium of like-sized spheres, the microscopic and macroscopic viscosities being identical. In this form it was applied to the anomalous dispersion of electromagnetic waves, and yielded for the molecular polarizability at a linear frequency ν, P_ν, the following expression:

$$\frac{M}{\rho}\cdot\frac{\epsilon-1}{\epsilon+2} = P_\nu = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3kT}\cdot\frac{1}{1+2\pi i\nu\tau}\right), \quad (1)$$

where ϵ is the dielectric constant at the frequency ν, M/ρ the gram formula volume, N Avogadro's number, α the optical polarizability, μ the electric moment, and τ the thermal relaxation time which Debye writes

$$\tau = 4\pi\eta r^3/kT. \quad (2a)$$

This is the time in which a molecule has, on an average, rotated 1 radian because of Brownian shocks. The exact numerical value is therefore of little importance, and the quantity has significance only in order of magnitude. In this sense Debye's interpretation of the anomalous dispersion of radio waves has been wholly successful, and is confirmed satisfactorily by the persistence of the electro-optical Kerr effect.

It is perhaps worth while to show at once by a simple approximate calculation that τ also has significance in the crystallization of a melt. As a crystal grows in an undercooled liquid it encounters chaotic orientation and leaves behind it perfect order. Thus in the process of crystallization the average molecule must be turned through $\pi/2$ radians. The average time necessary to effect this by thermal means will be[17]

$$\tau_0 = 2\pi^2\eta r^3/kT \quad (2b)$$

to the degree of approximation discussed above.

[16] P. Debye, *Polar Molecules* (The Chemical Catalog Company, 1929), p. 83 ff.

[17] J. Frenkel, Physik. Zeits. Sowjetunion **3**, 498 (1932) has proposed a somewhat similar argument, but without numerical examples.

If, at very low temperatures, the retardation of the linear crystallization velocity be considered wholly due to viscosity the velocity becomes

$$v_{\lim} \doteq 2r/\tau_0 = kT/\pi^2\eta r^2. \quad (3)$$

This relationship yields for glycerin, apparently the only substance for which reliable measurements for viscosity[18] and crystallization velocity[19] are at present known, taking $r = 5\times10^{-8}$ cm:

Temperature °K	253	248	243	238	233	228
τ_0 (sec.$\times10^4$)	0.86	1.9	5.0	13	36	111
v obs. (cm sec.$^{-1}\times10^5$)	7.3	5.2	3.3	1.7	0.60	0.1
$v_{\lim}$ calc. (cm sec.$^{-1}\times10^5$)	116	53	20	8	3	0.8

Over the last fifteen degrees the agreement is satisfactory between the measured and calculated values if the extremely approximate character of the argument is recalled. Lack of agreement at higher temperatures is to be expected, since the crystallization velocity is there determined by wholly different factors which the work of Volmer[19] and Stranski[20] has made intelligible. There is every reason to suppose that below 228°K the velocity of crystallization will proceed approximately in accordance with (3) and that from the standpoint of this property the "transition temperature" T_g will be traversed without discontinuous change, provided, of course, that no discontinuous change in the viscosity occurs.

It is necessary to inquire, therefore, if the viscosity of the liquid shows any abnormal change in the neighborhood of T_g. It appears that sufficient data are now available to answer this question unequivocally in the negative. T_g is generally admitted to occur when the viscosity is in the neighborhood of 10^{13} poises for a reason which will become apparent in the subsequent discussion. Lillie[9] has shown conclusively that, with several technical glasses, the viscosity-temperature curve is perfectly smooth to at least 10^{15} poises. Parks, Barton and Richardson[21] have

[18] G. Tammann and W. Hesse, Zeits. f. anorg. allgem. Chemie **156**, 245 (1926).

[19] M. Volmer and M. Marder, Zeits. f. physik. Chemie **A154**, 97 (1931).

[20] I. N. Stranski and R. Kaischew, ibid. **B26**, 100, 317 (1934).

[21] G. S. Parks, L. E. Barton, M. E. Spaght and J. W. Richardson, Physics **5**, 193 (1934).

measured the viscosity of glucose to 10^{14} poises with a similar result. Rencker,[12] by a somewhat less elegant method, has obtained similar information well below the "transition temperature" for selenium and boron sesquioxide glasses and for two resin plastics. In all cases which have been investigated to date, therefore, the "abrupt change in viscosity," which is sometimes referred to by writers on the transition point, is entirely absent.

Another matter arises in connection with these viscosity measurements which may as well be treated at once. The data of Parks, Barton and Richardson,[21] which deal with freshly prepared samples of glucose, conform to the relation apparently first interpreted by de Guzman,[22]

$$d \ln \eta / d(1/T) = \text{const}, \qquad (4)$$

when $\eta \geqq 10^{10}$ poises. Similarly the earlier results of Lillie[23] conform to (4) when $\eta \geqq 10^{9}$ poises. The results of Rencker, although not translatable into c.g.s. units, show a similar conformity throughout. The viscosity-temperature dependence expressed by (4) is that of a liquid of constant degree of "association." The constant of the equation is then the ratio of the "latent heat of fluidification" and the gas constant, and its constancy merely indicates that the molecular weight of the liquid is unchanged with temperature. Conformity to (4) indicates, therefore, that during the time necessary for carrying out the viscosity determinations no change in association takes place in the various glasses. Such behavior is, however, specifically required by (3), since the time of molecular rearrangements by thermal means becomes a matter of hours when $\eta \geqq 10^{10}$. Lillie[9] has very beautifully demonstrated that the association of molecules continues even at very high viscosities if sufficient time is allowed, and that the relation of the degree of association to temperature is then exactly the same in the region of T_g as it is at higher temperatures. In other words, for the association of molecules as well as for the linear crystallization velocity the thermal relaxation time plays a dominant part. This conclusion appears, unfortunately, wholly to undermine the interpretation given by Kobeko and his collaborators[3–7] to their measurements, since they have assumed a variable association throughout, and have allowed insufficient time for the degree of association to change at high viscosities.

A very serious objection may be advanced on the basis of a molecular-kinetic argument against the use of large relaxation times in the sense demanded by (3). Although slow processes of rotation and flow are commonplace occurrences with substances of high viscosity as, for example, the gradual disappearance of birefringence due to strain and shifts in the ice-point of thermometers, the movements of the individual molecules participating in these group movements must be extremely rapid. An analogy, suggested by the recent treatment of viscosity as a reaction rate given by Eyring,[24] may be drawn with the behavior of molecular hydrogen and oxygen at room temperatures: an exceedingly small fraction of the molecules react but those which react do so with great rapidity. Thus the reaction rate gives an indication of the average behavior of the molecules, since it gives the average rate at which water is being formed. It is, however, wholly incorrect to suppose that all of the molecules present are combined to the extent of a very small fraction. Similarly it is incorrect to interpret (3), in liquids of high viscosity, as indicating that the molecules are rotating extremely slowly, varying about a small mean angular velocity by some probability distribution. The relaxation time is merely the reciprocal of a quantity closely resembling a reaction rate, and may therefore be employed with value to characterize the average flow or rotation of a group of molecules, although it cannot be employed for the description of the behavior of any one of them. It must also be remembered that the extent of association of the liquid may also be varying with time so that the molecular radius has no clear-cut meaning. In spite of these objections the conception of the thermal relaxation time will be repeatedly employed below because of its simplicity, and because it is believed that it represents successfully the relation between the group behavior of the molecules and the viscosity.

[22] J. de Guzman, Anales, soc. espanola fys. y quim. **11**, 353 (1913).
[23] H. R. Lillie, J. Am. Ceram. Soc. **14**, 502 (1931).
[24] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

The Liquid-Glass Transition

It will be convenient first to consider the vitrification of an ideal or "normal" liquid, and then to relate the behavior deduced from this to the various glasses which have been studied, and which present a somewhat more complicated picture. An ideal liquid is, for this purpose, one in which aggregation of molecules does not take place, and which, therefore, obeys (4) over a wide temperature range. It may nevertheless be supposed to have a small permanent dipole moment as, for example, has chloroform. The fact that such a liquid would be most difficult to vitrify without crystallization need not concern us.

The dielectric constant of the idealized liquid will show the phenomenon of anomolous dispersion in conformity with the real part of (1). That is to say that at any given frequency the "transition temperature" will occur when $2\pi\nu\tau \cong 1$, and will be, from (2a)

$$T_g = 8\pi^2\eta r^3\nu/k \qquad (2c)$$

within the limit of applicability of the Debye interpretation. A few degrees above this temperature the dielectric constant will have a value characteristic of the liquid, and a few degrees below that characteristic of the amorphous solid. In this case one may further state that, at two different temperatures, by combining (2c) and (4)

$$\frac{T_{g1}}{T_{g2}} = \frac{\eta_1\nu_1}{\eta_2\nu_2} = \frac{\nu_1}{\nu_2}\exp\left(\text{const}\cdot\frac{T_2-T_1}{T_1T_2}\right). \qquad (5)$$

Thus the frequency at which the transition appears to take place will be lower the lower the temperature. At sufficiently high frequencies the dielectric constant will exhibit its glassy value even when the liquid is perfectly fluid. If one takes as T_g the point where the viscosity of the liquid has reached 10^{13} poises the dielectric constant will still be that of the liquid for very slowly alternating fields (of the order of one cycle in 10 days if r is 3×10^{-8} cm and T_g is 300°K). The maximum power loss in the "technical range" (60 cycles per second) will then appear in a dielectric of a viscosity of about 10^5 poises.

Turning now to experimental evidence there appear to be ample, if somewhat unsystematic, data for the support of this application of Debye's theory. Thomas[25] has found for the dielectric constant-temperature curve of glucose that the maximum slope occurs at a temperature some 15°C lower at 92 kc than at 2600 kc, which roughly accords with the viscosity data.[21] Kobeko[3] and Kobeko and Kuwschinsky[5] report similarly that the change of the dielectric constant occurs at a higher temperature than the abrupt change in the thermal expansion coefficient. Increasing association with decreasing temperature is reported, and this naturally obscures the simplicity of the picture outlined above. It is apparent that, except at relatively low viscosities, the time variation of the dielectric constant over long periods must be measured along with its temperature variation if the results are to be interpreted in any quantitative manner. It is also clear, however, that the "transition temperature" is not a fixed point for the dielectric constant, but varies as the rate of making the measurement (i.e., the frequency of the field) is varied.

Turning now to the heat capacity of the idealized liquid a very similar picture presents itself, obscured only by the customary method of measurement. Whereas the dielectric constant is ordinarily measured by an alternating field, the heat capacity is measured by adding a small measured quantity of heat, waiting for temperature constancy, and measuring the rise of temperature. Such a process has, of course, a *characteristic frequency* closely analogous to a slowly alternating field, and determined roughly by the reciprocal of the time allowed for the attainment of temperature "equilibrium."[25a] Since, in calorimetric work, these characteristic frequencies are extremely small (i.e., of the order of 10^{-3} sec.$^{-1}$) the point at which the "transition temperature" for the heat capacity will be observed will lie far below that for the dielectric constant. Since the reason for the change in the heat capacity lies in the rotational-vibrational rates of excitation and has no connection with the dipole moment, no simple relationship like (5) between the electrical and thermal "transition temperatures" can be written even for an idealized liquid. The statement may, however,

[25] S. B. Thomas, J. Phys. Chem. 35, 2103 (1931).

[25a] This conception may perhaps be clarified if the customary calorimetric measurement is considered to be a quarter of an uncompleted cycle of heating and cooling.

confidently be made that the transition will occur at a higher temperature the higher the characteristic frequency of the measurement.

Thus the full force of the statement by Parks and his associates quoted in the introduction may be realized. Decreasing the frequency of a calorimetric measurement from 10^{-3} to 10^{-4} sec.$^{-1}$ means a change from 20 minutes to 4 hours, and already raises almost insuperable obstacles of heat loss. Conversely increasing it from 10^{-3} to 10^{-2} sec.$^{-1}$ allows only 2 minutes for heat distribution, and invalidates the calorimetric method entirely. A way out of this difficulty appears to present itself in measurements of the velocity or absorption of sound.[26] A complete theory for the propagation of sound in very viscous media presents certain difficulties which need not here be discussed. It is sufficient to say that, in the simplest case,[26] the heat capacity in a cyclic process of frequency ν comports itself in accordance with the relation

$$C_\nu = C_\infty + (C_0 - C_\infty)/(1 + 2\pi i \nu \tau), \qquad (6)$$

where C_0, C_ν, and C_∞ are the heat capacities at the frequencies 0, ν and ∞, respectively. Thus a very wide range of frequencies of measurement become available. The relaxation time τ is, in this case, the reciprocal of the sum of the rates of excitation and de-excitation of the frequency dependent part of the heat capacity $C_0 - C_\infty$, and hence τ of (6) and τ of (1) bear no relation to each other. A numerical example to illustrate this point is fortunately at hand. Parks and Thomas,[27] using the Nernst calorimeter and heating at about 3° per hour, found that the point of maximum slope of the heat capacity-temperature function (i.e., the midpoint of the heat capacity "transition") came at about 7°C. At this temperature a linear extrapolation of the $\log \eta$ against $1/T$ curve[21] gives a viscosity of some 10^{18} poises. At 10^{18} poises the relaxation time of a particle of 5×10^{-8} cm radius at 280°K is of the order of 10^6 days from (2b), and hence far greater than the somewhat ill-defined characteristic time of measurement. It is evident, therefore, that the rotation of the molecules as a whole cannot possibly be concerned in the heat capacity change measured. A far more acceptable explanation is that at 7°C the rate of rotation of several groups in the molecule becomes of the order of the rate of measurement. Many cases are now known where groups continue to rotate even in a crystal lattice,[28] and such behavior in an amorphous solid seems equally plausible. Alternatively, it may be imagined that the frequency which is here measured characterizes the rate of excitation of certain vibrational modes of the glucose molecule. The supposition that it cannot be due to rotation of the molecules as a whole is further supported by the magnitude of the heat capacity change during the transition, which is reported to be some 40 cal. per gram formula weight, and must, therefore, be the result of the loss of many degrees of freedom. It is clear, then, that the relaxation time characterizing the heat capacity and that characterizing the dielectric constant are of different orders of magnitude.

A large number of other properties, however, which are concerned with the transport or rearrangement of molecules, may be expected to show the "transition temperature" at a point determined by the time of measurement and by a thermal relaxation time analogous to that given by the dielectric constant. These are, for example, the rate of disappearance of birefringence due to strain, the thermal coefficient of expansion, and the closely related refractive index. Phenomena of hysteresis are to be expected in all of these properties as, indeed, in all properties when the viscosity is high. The hysteresis will increase at the beginning of the "transition range" as the temperature is lowered, and then apparently diminish in the region of very high viscosities owing to the fact that the relaxation time exceeds by greater and greater amounts the time of measurement. Finally, no further change of the position of the molecules will be appreciable, and the liquid will have vitreous properties. Change of position will be unobservable when the time of measurement is inferior to the relaxation time by some two orders of magnitude

[26] Acoustical theory pertinent to this problem was first written in analogy to optical theory by A. Einstein, Sitz. Ber. Akad. 380 (1920). It has since been extensively developed by other writers, but only for gases.

[27] G. S. Parks and S. B. Thomas, J. Am. Chem. Soc. **56**, 1423 (1934).

[28] Cf. J. Errera, J. de phys. et rad. **5**, 304 (1924); C. P. Smyth and C. S. Hitchcock, J. Am. Chem. Soc. **54**, 46 (1931).

in a relationship of the type of (6). At 10^{13} poises viscosity the relaxation time of a molecule is something like 5 days depending, of course, to some extent on its radius and the absolute temperature. Thus for measurements consuming an hour or less the liquid will be vitreous when this viscosity has been attained. Measurements of viscosity changes over long periods of time, which have been cited above,[9, 21] are ample proof that constancy in properties of the "vitreous state" is apparent rather than real. The practical bearing of this argument on annealing is obvious: a glass should be held at a temperature where it flows slowly for a time considerably greater than its relaxation time, and then cooled as rapidly as possible without shattering. This is essentially the procedure recommended by Adams and Williamson.[29]

One further aspect of the liquid-glass transition must be discussed. This is the thermal change, analogous to a heat of fusion, which some writers believe to accompany the liquefaction of glass. If any such absorption of heat actually occurs there is, of course, good reason to suppose with le Chatelier[1] that an allotropic change has taken place, and to refer to a "vitreous state of aggregation" as apart from a very viscous liquid. Any structural change involving the liberation of measurable heat on cooling should, however, manifest itself by a discontinuity in the viscosity-temperature function as, for example, with the mesomorphic transitions. Since the wide variety of substances cited above show no such discontinuity, it becomes necessary to examine closely the experimental conditions under which heat evolution and absorption are found. Two types of experiment lead to this interpretation. The first, due to Tool and Valasek,[30] employs a differential thermocouple method by which the sample and a reference substance free from transitions in the temperature range in question are slowly heated in a furnace. Below the "transition region" the substances lag behind the temperature of the furnace by an amount directly proportional to their heat capacity and inversely proportional to their heat conductivity. Absorption of heat is shown by a sudden increase in the relative lag of the vitreous sample, but such an effect would also be caused by a sudden increase of heat capacity. It is found, however, that the new lag is not maintained by the now liquid sample but slowly diminishes as the temperature continues slowly to rise. Thus the curve of the differential temperature of reference substance and glass plotted against the temperature shows a sharp drop, and a clear although very shallow minimum. This might indicate an absorption of heat, but might also be due to the increasing heat conductivity of the softened glass. Both Tammann[31] and Rencker,[12] who have studied these differential curves in detail, declare themselves convinced that no "latent heat of transformation" exists, and the argument given above corroborates their conclusion. The second type of "latent heat" effect has been found by Parks and his associates in their calorimetric work; their data on the heat capacity of glucose glass illustrate this vividly.[27] In a Nernst calorimeter, at a slow rate of heating, the heat capacity transition gave the regular S-shaped curve described by the real part of (6), with its point of maximum slope at about 7°C. No "latent heat" effect is apparent. In a radiation calorimeter, at a much higher rate of heating, the point of maximum slope shifted to 32°C and an enormous maximum appeared in the apparent heat capacity. The reason for this behavior becomes clear from considerations of viscosity: The glass does not show a change of heat capacity until the product of its thermal relaxation time and the rate of heating is nearly unity, and then catches up on its heat content very rapidly. Since, in order to be brought to a higher temperature and become a liquid a certain amount of heat must be absorbed the heat capacity appears to go through a maximum at rapid rates of energy input. Since both these types of measurement are dynamic and have been shown to depend strongly on the rate of heating (or cooling), and since the results of both are readily explained without the introduction of a "latent heat of transition," it appears misleading to employ this conception.

[29] L. H. Adams and E. D. Williamson, J. Frank. Inst. 190, 597, 835 (1920).

[30] A. Q. Tool and J. Valasek, Bur. Stand. Sci. Pap. No. 358 (1920).

[31] G. Tammann, *Glaszustand* (Leipzig, 1930).

Devitrification

Tammann, in his classical researches on crystallization,[32] has shown that devitrification may occur homogeneously (i.e., throughout the interior of the liquid) by the formation of numerous small crystals. Volmer[19] and Stanski[20] have applied fluctuation theory to the process, and a complete and acceptable picture for its mechanism has emerged. From what has been said above, however, it is clear that the viscosity must be relatively low for this to occur. In ordinary laboratory glass for which the value of 10^{70} poises at room temperature has been given by a glass technologist,[33] the relaxation time is greater than 10^{50} years, and the formation of crystalline germs is wholly precluded. However, devitrification of soda lime glasses within 10 years is a common occurrence. Thus a heterogeneous mechanism for this process (i.e., some process which occurs at an interface) which greatly lowers the relaxation time must be found. In line with this deduction an x-ray investigation on the crystallinity of a Roman glass (supposedly from the II century) a XIV century French glass, a 20-year old soda lime glass, and a freshly fused sample of Pyrex revealed no great differences in the interior properties of the four, but showed that surface crystallinity of all but the Pyrex sample was conspicuously present.

Several mechanisms for the formation of crystals at an interface will briefly be discussed.

(1) Exchange adsorption

It is now generally agreed, owing largely to the work of Langmuir, that a glass in air is surrounded by a thin film of water molecules. It is also recognised that, in adsorption studies on glass, the presence of water vapor leads to irreversible changes of the surface. The generally accepted mechanism by which these changes are produced involves the exchange of sodium ions for hydrogen ions by the silicates present in the glass, the homopolar silicic acid ("silica gel") so formed remaining on the glass surface throughout subsequent changes. There is no reason to question this explanation, and it provides a mechanism whereby the glass may rapidly be coated with a layer of different thermal expansion coefficient and consequently tend to shatter on heating. The depth to which this action penetrates will of course depend on time, temperature, and concentration of water. The silicic acid so formed is initially amorphous, but may be expected to change slowly to a crystalline modification, since this behavior is typical of the hydrous oxides.

(2) Surface solution

The vapor pressure of most glasses is so low that the evaporation and recondensation of molecules on the surface can scarcely be considered a plausible mechanism by which devitrification may be brought about. Furthermore, although in the vapor phase they are freed from excessive internal friction and able to rotate, the experiments of Tammann[32] show that molecules tend to condense in an amorphous, not a crystalline form in spite of the fact that the large energy at the glass-air interface would tend to produce orientation. Evaporation into and condensation from some solvent, on the other hand, provides a means for a far greater amount of material may leave the surface and recondense per unit time. It has been known since the time of Mitscherlich that vitreous selenium changes slowly on its surface to the red crystalline variety when immersed in carbon bisulfide. Similarly Parks, Huffman and Cattoir[34] mention that traces of water greatly promote the devitrification of glucose. Indeed it has been found in this laboratory that many inorganic and organic glasses which are water soluble devitrify rapidly over water whereas they remain entirely stable for long periods in a desiccator over phosphorous pentoxide. Sometimes a very thin coating of a nonvolatile substance in which the glass is insoluble will prevent its devitrification by this mechanism. This is perhaps the most plausible mechanism for the devitrification of laboratory glass at room temperature.

(3) Presence of overheatable germs

The possibility that crystal nuclei may persist above the temperature of melting was first

[32] G. Tammann, *Kristallisieren und Schmelzen* (Leipzig, 1903).
[33] F. W. Preston, J. Am. Chem. Soc. **15**, 365 (1932).
[34] G. S. Parks, H. M. Huffman and F. R. Cattoir, J. Phys. Chem. **32**, 1366 (1928).

demonstrated by Othmer.[35] His experiments show that the number of crystal nuclei formed in several undercooled liquids depends on the previous thermal history of the melt, decreasing as the temperature of the melt is raised above the melting temperature. Tammann[36] has considered it due to alterations in the internal condition of the liquid. Several cases have, however, recently been reported where similar phenomena may be produced by the inclusion in the liquid of small quantities of an adsorbing substance.[37] These appear to be explicable by the hypothesis that the adsorbate has two forms of different energy content and structure, one of which resembles a deformed crystal lattice in its orientation, and the other of which has the orientation of the undercooled liquid. Nuclei covered with the so-called "crystalline adsorbate" are capable of acting as crystallization centers as if they were actual crystals, but the phenomenon clearly belongs to the realm of heterogeneous devitrification because it cannot occur without the presence of the adsorbent. The general aspects of this type of crystallization have been sufficiently dealt with, and it remains only to discuss its appearance in glasses. Such a mechanism can hardly be held accountable for the devitrification of laboratory glassware, since crystal growth at room temperature must be fantastically slow.

It is perhaps worth pointing out, however, that the statement of Littleton[38] "The problem of avoiding devitrification is then simply one of determining the liquidus temperature and keeping the glass above this during any protracted heating" may perhaps require modification. If the walls of the vessel containing the molten glass are capable of acting as adsorbents for the crystalline modification of a component of the glass, temperatures much higher than the liquidus temperature may be necessary in order to destroy nuclei capable of initiating crystallization.

(4) Flow phenomena

Devitrification due to flow, although familiar to the glass-blower, has apparently been mentioned in only one publication,[39] and then given only passing attention. A laboratory demonstration of this is practiced by the Röntgen-ray technician who wishes to secure a crystalline thread of glass. He takes a sample of glass which is already somewhat devitrified, heats this in a blast flame, and pulls it into a fine filament. When the flow of glass is almost at an end he pulls especially strongly, rupturing the filament at its weakest point. The surface of the resulting thread of glass is microscopically rough, and the thread as a whole shows a strongly crystalline x-ray pattern. In order to explain devitrification under these conditions it is necessary to suppose that the molecules of the glass are unsymmetrical in shape; a similar assumption appears to be necessary for the explanation of strain birefringence. If this is the case they will orient themselves in lines of equal flow velocity in a manner similar to the vanadium pentoxide sols described by Freundlich and his associates.[40] This orientation evidently greatly assists crystallization in the case of silicate glasses, although it need not be expected to do so in general. After the glass has set the orientation persists owing either to the greater thermodynamic stability of the crystalline state, to the magnitude of the relaxation time, or to both. It appears probable that surface crystallization proceeding from scratches made by a diamond on glass owes its origin to similar orienting forces under the enormous pressure of the diamond point. Tabata,[41] who has reported these experiments, explains them by an argument based on surface energy which is not convincing. The recent work of Bridgman[42] on polymorphism under pressure and torsion indicates that orientations of this type are to be expected as a general property of unsymmetrical molecules.

I am indebted to Mr. R. H. Ewell for acquainting me with much of the literature of glasses.

[35] P. Othmer, Zeits. f. anorg. allgem. Chemie **91**, 209 (1915).
[36] G. Tammann, *Aggregatzustande* (Leipzig, 1922).
[37] W. T. Richards, J. Am. Chem. Soc. **54**, 479 (1932).
[38] J. T. Littleton, J. Am. Ceram. Soc. **17**, 43 (1934).
[39] K. Endell, Ber. Deuts. Keram. Gesell. **13**, 115 (1932).
[40] P. Dieselhorst and H. Freundlich, Physik. Zeits. **17**, 117 (1916).
[41] K. Tabata, J. Am. Ceram. Soc. **10**, 6, 145 (1927).
[42] P. W. Bridgman, Phys. Rev. **48**, 825, 893 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Structure of Potassium Tetroxide

Up to the present time the structure of potassium tetroxide has not been determined. E. W. Neuman[1] on the basis of magnetic measurements concludes that this compound contains O_2^- ions and that its formula is KO_2. Klemm and Sodomann,[2] however, have shown that the formula K_2O_4 containing the ion $O_2^{--} \cdots O_2$ is also consistent with the magnetic data because of the paramagnetism of the oxygen molecule. Therefore the structure of potassium tetroxide cannot definitely be stated by the study of magnetic properties only.

At the suggestion of Professor J. A. Kasarnowsky we have undertaken an x-ray investigation of this substance. A pure sample of potassium tetroxide was prepared in this laboratory by S. Reichstein who also determined its density. By taking powder photographs and using the Hull-Davey charts we were able to establish a tetragonal face-centered lattice of the calcium carbide type.[3] The elementary cell contains four potassium atoms and eight oxygen atoms and has the following dimensions: $\mathbf{c}=6.72$A, $\mathbf{a}=5.70$A, $\mathbf{c/a}=1.178$. The density calculated from the dimensions of the unit cell is $\delta_{calc}=2.15$ in agreement with the density value $\delta_{meas}=2.158$ measured in a pycnometer. The space group is $D_{4h}^{17}-F4/\mathbf{mmm}$. The coordinates of the four potassium atoms are 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$ and those of the eight oxygen atoms are $\frac{1}{2}00\pm U, 0\frac{1}{2}0\pm U, 00\frac{1}{2}\pm U, \frac{1}{2}\frac{1}{2}\frac{1}{2}\pm U$. By comparing the calculated and observed intensities we obtained for the parameter U the value $U=0.095$, which corresponds to a distance between adjacent oxygen nuclei of $d_{O-O}=1.28\pm0.07$A.

The structure we have found for the potassium tetroxide lattice is quite analogous to that of SrO_2 and BaO_2[4] and may be considered as a rocksalt lattice elongated in one direction because of the shape of the anion. The SrO_2 and BaO_2 lattices, however, contain doubly charged oxygen ions O_2^{--} while KO_2 contains singly charged ions O_2^-. These data allow us to conclude that the formula of the highest potassium oxide is KO_2 in concordance with the views of Pauling and Neuman.[1]

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April 25, 1936.

[1] E. W. Neuman, J. Chem. Phys. **2**, 31 (1934).
[2] W. Klemm und Sodomann, Zeits. f. anorg. u. allg. Chem. **225**, 273 (1935).
[3] M. v. Stackelberg, Zeits. f. physik. Chemie **B9**, 437 (1930).
[4] J. D. Bernal, E. Djatlowa, J. Kasarnowsky, S. Reichstein and A. G. Ward, Zeits. f. Krist. **A92**, 344 (1935).

Note on Dipole Moments of Molecules in Solution

The suggestion has been made by H. O. Jenkins* that the moment of a polar molecule dissolved in a non-polar solvent fluctuates about a mean μ_0 in a manner given by

$$dP(\mu) = Ce^{-(\alpha/T)(\mu/\mu_0-1)^2}d\mu \qquad (1)$$

so that the observed moment is

$$\overline{\mu^2}_{obs} = \frac{C\int_{-\infty}^{+\infty} e^{-(\alpha/T)(\mu/\mu_0-1)^2}\mu^2 d\mu}{C\int_{-\infty}^{+\infty} e^{-(\alpha/T)(\mu/\mu_0-1)^2}d\mu}, \qquad (2)$$

where $dP(\mu)$ is the chance the moment has a value between μ and $\mu+d\mu$; μ_0, C, and α are constants characteristic of the dipole and the solvent and T is the absolute temperature. A theoretical derivation of expression (1) is given below.

(Jenkins showed that if one assumes the dipoles in a molecule such as *p*-dinitrobenzene behave independently with regards to this fluctuation and further that the latter is of a period which is relatively low compared to that of the orientation of the dipole in the local field, he can account for the existence of a moment in such a symmetrical molecule. Also, he can accurately predict the value to be expected for symtrinitrobenzene were he to use the available data for the dinitro compound to calculate the constant μ_0. The success of the predictions so made for the above case and for quinone, beryllium acetylacetonate and basic beryllium acetate provide support for Eq. (1) from an empirical standpoint. Attention is called to the fact that the invariant nature of the polarization with respect to the temperature is also thus accounted for.)

To explain the observed discrepancy between the values for the dipole moment as obtained from the dielectric constant measurements on the gas and on dilute solutions of the polar substance in a nonpolar solvent, K. Higasi[1] considered the change in μ_{gas} due to the induced moment in the medium immediately surrounding an ellipsoidal polar molecule. He concluded that

$$\mu_{sol}=\mu_{gas}(1+2\pi qAn),$$

where A is a function of the shape of the solute molecule, the position of the dipole in it, etc., q is the polarizability per molecule of the solvent and n is the number of solvent molecules per unit volume. For the purpose of the present discussion it is not necessary to specify the dependence of μ_{sol} so completely; it is sufficient to state

$$\mu_{sol}=\mu_{gas}(1+fn), \qquad (3)$$

where f is a function characteristic of the solute and solvent. It can be shown that if one circumscribes around the dipole a sphere large enough just to include the solute molecule the contribution of the material outside this sphere to the change in μ_{gas} vanishes. To evaluate f one must consequently integrate the induced polarization over the volume included between the surface of the polar molecule and that of the circumscribing sphere. Since this volume is of molecular dimensions, n should not be given the averaged macroscopic value but one which fluctuates appreciably about a mean n_0. Hence μ_{sol} of Eq. (3) is really an instantaneous value (μ). In the simple argument to be given below it is implicitly assumed that whatever the instantaneous n happens to be, it is uniform for the entire volume over which the intergration is performed. Further consideration will show, however, that the final equation is not necessarily restricted by this assumption since the form of f is left unspecified.

Let dN be the number of molecules of the solute having between n and $n+dn$ molecules of the solvent per unit volume in their shell of influence. The well-known expression for such a fluctuation[2] states

$$dN = B_0 e^{-(b/kT)(n-n_0)^2} dn,$$

where B_0 is a normalizing factor and b depends on the nature of the solute and solvent molecules. From (3)

$$(n-n_0)^2 = (1/f\mu_0)^2(\mu-\mu_0)^2.$$

Therefore,

$$dN = Ce^{-(\alpha/T)(\mu/\mu_0-1)^2} d\mu,$$

where

$$C = B_0(1/f\mu_0) \quad \text{and} \quad \alpha = (b/k)(\mu_0/f\mu_0)^2.$$

Eq. (2) follows immediately.

Thanks are due Professor Pauling and Dr. Jenkins for a number of interesting discussions.

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June 15, 1936.

* (Private communication. Manuscripts to appear in the J. Chem. Soc.)

[1] K. Higasi, Tokyo, Proc. Inst. Phys. Chem. Research **28**, 284 (1936).
[2] R. C. Tolman, *Statistical Mechanics*, p. 230.

Concerning the Amorphous and Crystalline Forms of Rubber Hydrocarbon

The coefficients of thermal expansion and the heat capacities of rubber hydrocarbon both in an amorphous and in a so-called crystalline form have been recently reported in two papers by Bekkedahl and Matheson.[1] According to these investigators, the amorphous form undergoes a transition of the second order in the neighborhood of 199°K. Above this temperature they found a rather abrupt increase of approximately 205 percent in the volume coefficient of thermal expansion and one of about 38 percent in the heat capacity. These phenomena are strikingly similar to those found in numerous studies on glasses in this laboratory and especially in the recent investigation on polyisobutylene by Ferry and Parks.[2] Thus, with the particular sample of polymerized isobutene employed, the *transition region* centered around 197°K and the subsequent increases in volume coefficient and heat capacity were 200 and 32 percent, respectively.

Bekkedahl and Matheson found that, by cooling the amorphous rubber hydrocarbon to about 230°K and then permitting it to warm up slowly over a period of days, their material could be obtained in a "crystalline" form. These "crystals" melted at 284°K with a heat of fusion of 4.0 cal. per gram. They also exhibited the previously-mentioned second-order transition at about 199°K but with somewhat smaller subsequent increases with rising temperature, i.e., about 165 percent increase in the volume coefficient of thermal expansion and 28 percent in the heat capacity. Two facts appear surprising and highly significant with these "crystals": (1) The value of the heat of fusion which is extremely low compared with the figures of 20 to 54 cal. per gram hitherto reported for various aliphatic hydrocarbons melting near room temperature,[3] and (2) the duplication of the second-order transition found previously for the amorphous rubber hydrocarbon.

The writer of this communication feels that these two facts can best be explained by the supposition that Bekkedahl's "crystals" really represent a mixture of amorphous and crystalline rubber hydrocarbon. Assuming that the second-order transition is solely due to the amorphous hydrocarbon, he estimates the percentage of this in the so-called crystals to be about 80 from the relative increases of the volume coefficients above 199°K. Similarly from the relative increases of the heat capacities above this transition, he estimates 71 percent amorphous material in the "crystals." These estimates check only roughly but in this connection it is important to note that the two types of measurements were made upon different samples and that the sample used for the specific heat measurements was contaminated with 2.8 percent oxygen. The presence of such a large percentage of amorphous substance in this "crystalline" form is not really surprising in view of the high molecular weight of rubber hydrocarbon and the probability that the material contains a variety of molecules representing various degrees of polymerization of C_5H_8. In fact, similar but not such extensive contamination of the crystalline form with amorphous material has previously been observed in this laboratory with such relatively simple substances as ethyl alcohol, *n*-amyl alcohol,[4] and lactic acid.[5] In the case of the last named, Parks, Thomas and Light, on crystallizing the liquid, obtained a two-phase system with about 12 percent amorphous material.

On the basis of his hypothesis of 71 percent amorphous material in the rubber hydrocarbon crystals of Bekkedahl and Matheson, the writer has obtained from their data an estimate of 17.4 cal. per gram for the heat of fusion of pure crystals. This estimate is of the same order of magnitude as the values reported previously for many other paraffin and olefin hydrocarbons melting above 200°K.

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[1] Bekkedahl, Bur. Standards J. Research **13**, 411 (1934); Bekkedahl and Matheson, *ibid.* **15**, 503 (1935).
[2] Ferry and Parks, J. Chem. Phys. **4**, 70 (1936).
[3] See, for example, Parks and Huffman, Ind. Eng. Chem. **23**, 1138 (1931).
[4] Parks, Huffman and Barmore, J. Am. Chem. Soc. **55**, 2733 (1933).
[5] Parks, Thomas and Light, J. Chem. Phys. **4**, 64 (1936).

The Infrared Spectrum of Heavy Acid Solutions

Previous studies[1] have shown that all acids in aqueous solution absorb strongly at 5.6μ and at 2.4μ. As the position of the 5.6μ band was found to vary slightly with the acid in solution, this absorption was explained as arising from the association of an undissociated acid molecule with a water molecule, the association bond being through the hydrogen atom of the acid. The band at 2.4μ was interpreted as arising from the association of the hydrogen ion with the water molecule.

Similar studies have been made of the spectra of solutions of the heavy acids DCl, D_2SO_4, and D_3PO_4 in deuterium oxide. It has been found that the regions of characteristic absorption are 5.7μ and 3.4μ. The slight variation in position of the band near 5.6μ is to be expected if this absorption arises from an oscillation in which two whole molecules are involved. The presence of the band at 3.3μ in the deuterium-containing compounds is in excellent agreement with predictions based on mass differences if a deuterium ion is involved in the mechanism of absorption. The study of the spectra of these solutions is being continued in the region of shorter wave-lengths.

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E. K. Plyler and E. S. Barr, J. Chem. Phys. **2**, 306 (1934).

The Infrared Absorption of Rubber and Related Hydrocarbons

The infrared absorption spectra of rubber and certain related hydrocarbons have been studied by using extremely thin films of the samples as absorbing layers. In the spectra of styrene, isoprene, and cymene intense absorption bands appear at 3.4μ, 6.2μ, and 7.0μ and also weaker bands between 7μ and 9μ. These bands were common to most of the hydrocarbons studied. The principal variations in the spectra of the compounds mentioned above are found in bands whose positions vary between 5.5μ and 5.7μ in the different compounds. In the case of pure gum rubber a band was found at 5.8μ, and in a vulcanized rubber of low sulphur content corresponding absorption occurs at 6.0μ. At all other wave-lengths between 2.5μ and 9.0μ the absorption spectrum of rubber has a striking resemblance to that of isoprene, a result which is agreement with the chemist's model of the rubber molecule as a long chain of isoprene units. The absorption in the 5.8μ region probably arises from a mechanism which is intimately connected with the process of polymerization. The spectrum of polymerized butadiene contains strong bands at 5.5μ and 6.0μ and also less intense bands beyond 7.0μ, whose positions are not the same as those in the spectrum of natural rubber. Rubber hydrochloride has a very intense band at 8.4μ which is not characteristic of the other hydrocarbons studied.

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